SUPPORTING INFORMATION

Efficient chemical fixation of CO_2 promoted by bifunctional Ag_2WO_4/Ph_3P system

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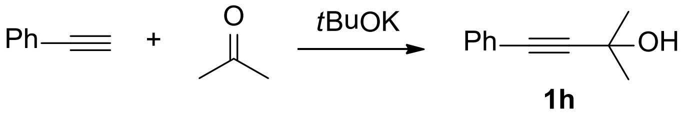
1. General Experimental Methods

1.1 General Information

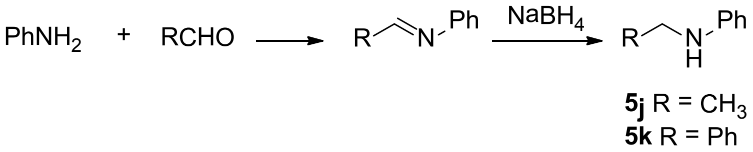
All reactions were carried out without any special precautions against air. All starting materials were obtained from TCI, Aladdin or Alfa Aesar and used as received. Ag_2WO_4 was purchased from Alfa Aesar. Carbon dioxide of 99.99% purity was commercially available. ^1H NMR spectra was recorded on 400 MHz spectrometers using $CDCl_3$ as solvent referenced to TMS (0 ppm) or $CHCl_3$ (7.26 ppm). ^{13}C NMR was recorded at 100.6 MHz in $CDCl_3$ and $CDCl_3$ (77.0 ppm) was used as internal reference. FT-IR was recorded on a Bruker Tensor27 FT-IR spectrophotometer with KBr pellets. High resolution mass spectrometry was conducted using a Varian 7.0 T FTICR-MS by ESI technique. GC analyses were performed on Shimadzu GC-2014, equipped with a capillary column (RTX-17, 30 m × 0.25 μm) using a flame ionization detector. Melting points were measured on an X4 apparatus and uncorrected. Mass spectra were recorded on a Shimadzu GCMS-QP2010 equipped with a RTX-5MS capillary column at an ionization voltage of 70 eV.

1.2 Procedure for the synthesis of 2-methyl-4-phenylbut-3-yn-2-ol.[1]



After anhydrous acetone (1.16 g, 20 mmol), ethynylbenzene (2.09 g, 20 mmol), and potassium *t*-butoxide (2.21 g, 20 mmol) were well-mixed with agate mortar and pestle, the mixture was kept at room temperature for 20 min. The reaction product was mixed with 10% aqueous sodium chloride, filtered, washed with water, and dried to give as colorless crystal.

1.3 Synthesis of N-ethylaniline and N-benzylaniline.[2]



A mixture of an aldehyde (10 mmol), phenylamine (11 mmol) and Na_2SO_4 in CH_2Cl_2 (20 mL) was stirred for 2 h. The CH_2Cl_2 solution was concentrated under reduced pressure. The residue was dissolved in MeOH (20 mL), and treated with $NaBH_4$ (0.19 g, 5 mmol) at r.t. for 1 h. The mixture was concentrated, and the residue was dissolved in CH_2Cl_2 (25 mL), washed with water (3 × 10 mL), and dried with Na_2SO_4. The CH_2Cl_2 solution was concentrated under vacuum and the residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to give the desired products.

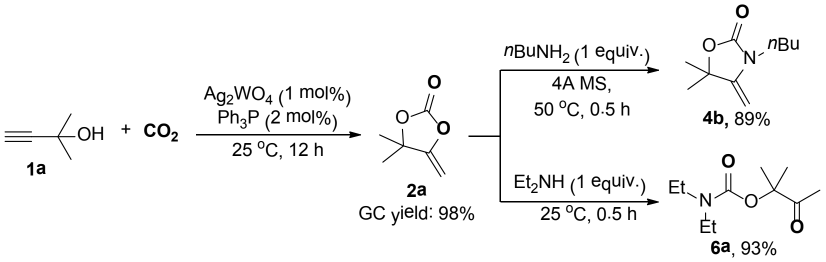
1.4 Synthesis of α-alkylidene cyclic carbonates by carboxylative cyclization of propargyl alcohols with CO_2.

Ag_2WO_4 (23.2 mg, 1 mol%), PPh_3 (26.2 mg, 2 mol%), and propargylic alcohols (5 mmol), was added to a Schlenk tube equipped with a magnetic stir bar. CO_2 balloon was consecutively introduced. Then the mixture was stirred at 25 °C for the desired time. Upon completion, the mixture was diluted with *n*-hexane (3×5 mL). The organic phase was collected then purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to give the desired products. The residue solid in the tube was Ag_2WO_4, which can be used directly in the next run.

1.5 Synthesis of 5-methylene-1,3-oxazolidin-2-ones or β-oxopropylcarbamates by three-component reactions of propargylic alcohols, (primary or secondary) amines and CO_2.

The reactions were conducted in a 25-mL oven-dried autoclave with glass tube inside equipped with magnetic stirring. Ag_2WO_4 (23.2 mg, 1 mol%), Ph_3P (26.2 mg, 2 mol%), propargylic alcohols (5 mmol), amines (primary or secondary amines, 5 mmol), 4Ǻ molecular sieves (only for primary amines, 50 mg), and CO_2 (0.5 MPa) were successively introduced and heated at 50 °C for 12 h. When the reaction completed, the vessel was cooled with an ice-bath, and the pressure was released slowly to atmospheric pressure. The residue was flushed with 3×5 mL diethyl ether and removed under vacuum. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to give the desired products.

1.6 Procedure for stepwise synthesis of typical 5-methylene-1,3-oxazolidin-2-one and β-oxopropylcarbamate.



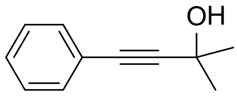
Ag_2WO_4 (23.2 mg, 1 mol%), PPh_3 (26.2 mg, 2 mol %), and propargylic alcohols (0.421 g, 5 mmol) were combined and sealed in an oven-dried 10-mL Schlenk tube equipped with a stir bar; CO_2 (balloon) was successively introduced and heated at 25 °C for 12 h. The yields were quantified by GC method. Then amines (primary or secondary amines, 5 mmol) (4Ǻ molecular sieves used only for primary amines, 50 mg) were successively introduced with a syringe and stirred at 50 °C for 0.5 h. Then, the reaction was cooled down to room temperature. The residue was flushed with 3×5 mL diethyl ether and removed under vacuum. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to give the desired products.

Reference

[1] H. Miyamoto, S. Yasaka, K. Tanaka, *Bull. Chem. Soc. Jpn.* **2001**, *74*, 185-186.

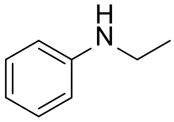
[2] K. Orito, M. Miyazawa, T. Nakamura, A. Horibata, H. Ushito, H. Nagasaki, M. Yuguchi, S. Yamashita, T. Yamazaki, M. Tokuda, *J. Org. Chem.* **2006**, *71*, 5951-5958.

2. Characterization Data for Substrates and Products



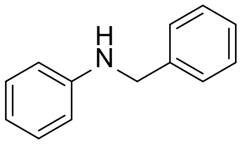
1h

Colourless solid (2.78 g, 88% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.42-7.41 (m, 2H), 7.30-7.29 (m, 3H), 2.09 (1H, OH), 1.62 (s, 6H) ppm.^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 131.6, 128.2, 122.7, 93.7, 82.1, 65.6, 31.5 ppm.



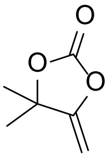
5j

Yellow oil (0.95 g, 78% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.20-7.15 (m, 2H), 6.70-6.67 (m, 1H), 6.60-6.58 (m, 2H), 3.50 (1H, NH), 3.16-3.11 (q, 2H), 1.25-1.22 (t, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 148.4, 129.2, 117.1, 112.7, 38.4, 14.8 ppm.



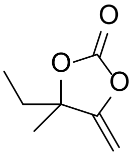
5k

Colourless solid (1.61 g, 88% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.39-7.35 (m, 4H), 7.32-7.30 (m, 1H), 7.22-7.19 (m, 2H), 6.77-6.73 (m, 1H), 6.68-6.66 (m, 2H), 4.35 (s, 2H), 4.10 (1H, NH) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 148.1, 139.4, 129.2, 128.6, 127.5, 127.2, 117.6, 112.8, 48.3 ppm.



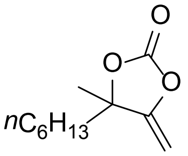
2a

Colourless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.75 (d, *J* = 4.0 Hz, 1H), 4.31 (d, *J* = 4.0 Hz, 1H), 1.59 (s, 6H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 158.6 (C=O), 151.2, 85.2, 84.6, 27.5 ppm. GC-MS (EI, 70 eV) *m/z* (%) = 128.10 (2.81), 85.10 (6.49), 84.10 (100), 83.10 (3.54), 69.10 (48.16).



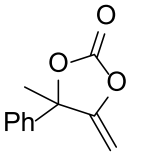
2b

Colourless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.80 (d, *J* = 4.0 Hz, 1H), 4.26 (d, *J* = 4.0 Hz, 1H), 1.94-1.70 (m, 2H), 1.57 (s, 3H), 0.97 (t, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 157.2, 151.4, 87.5, 85.4, 33.1, 25.7, 7.1 ppm. GC-MS (EI, 70 eV) *m/z* (%) = 143.10 (6.27), 113.05 (15.98), 98.10 (29.81), 83.05 (74.98), 70.10 (100).



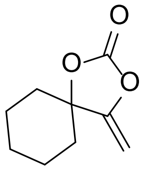
2c

Colourless oil. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 4.77 (d, J = 4.0 Hz, 1H), 4.26 (d, J = 4.0 Hz, 1H), 1.89-1.64 (m, 2H), 1.57 (s, 3H), 1.26-1.37 (m, 8H), 0.86 (t, 3H) ppm. ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 157.7, 151.5, 87.2, 85.4, 40.4, 31.4, 28.9, 26.3, 22.8, 22.4, 13.9 ppm. GC-MS (EI, 70 eV) m/z (%) = 199.15 ([M+H]$^+$, 1.19), 139.2 (13.21), 112.15 (35.48), 111.15 (50.99), 97.10 (67.92), 85.10 (29.83), 84.10 (44.50), 83.10 (72.10), 82.10 (29.07), 72.10 (75.49), 70.15 (92.82), 69.10 (100).



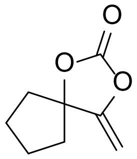
2d

Greenish-yellow oil. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.49-7.47 (m, 2H), 7.44-7.38 (m, 3H), 4.95 (d, J = 4.0 Hz, 1H), 4.48 (d, J = 4.0 Hz, 1H), 1.97 (s, 3H) ppm. ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 157.2, 151.0, 139.1, 129.0, 128.8, 124.5, 88.1, 87.0, 27.3 ppm. GC-MS (EI, 70 eV) m/z (%) = 146.10 (12.70), 131.10 (19.18), 118.15 (100), 117.15 (82.22), 103.10 (52.08), 78.10 (32.34), 77.10 (42.95).



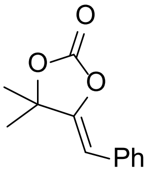
2e

Colourless oil. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 4.73 (d, J = 4.0 Hz, 1H), 4.28 (d, J = 4.0 Hz, 1H), 1.98-1.95 (m, 2H), 1.70-1.59 (m, 7H), 1.34-1.20 (m, 1H) ppm. ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 158.4, 151.2, 86.2, 85.3, 36.2, 24.0, 21.4 ppm. GC-MS (EI, 70 eV) m/z (%) = 124.10 (9.13), 109.10 (15.29), 95.10 (14.64), 82.10 (48.56), 81.15 (49.96), 80.10 (19.71), 67.10 (100).



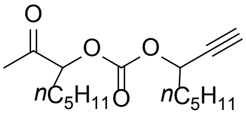
2g

Straw yellow oil. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 4.76 (d, J = 3.6 Hz, 1H), 4.33 (d, J = 4.0 Hz, 1 H), 2.18-2.22 (m, 2H), 1.81-1.92 (m, 6H) ppm. ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 157.6, 151.4, 94.1, 85.3, 40.5, 24.1 ppm. GC-MS (EI, 70 eV) m/z (%) = 110.10 ([M-44]$^+$, 5.53), 95.10 (15.23), 69.10 (5.64), 68.10 (76.55), 67.10 (100), 66.10 (24.16), 65.10 (6.24).



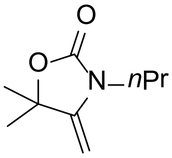
2h

Colourless oil. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.47-7.45 (m, 2H), 7.29-7.25 (m, 2H), 7.19-7.16 (m, 1H), 5.43 (s, 1H), 1.61 (s, 6H) ppm. ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 151.2, 150.7, 132.3, 128.6, 128.4, 127.5, 101.5, 85.5, 27.6 ppm. GC-MS (EI, 70 eV) *m/z* (%) = 204 (8.7), 160 (23.8), 145 (26.25), 132 (69), 117 (100), 115 (29.9), 91 (19), 89 (14).



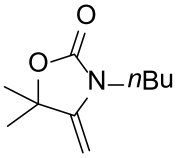
2i

Straw yellow oil. IR (KBr): *ν*/cm^{-1} 3287 (≡C-H); 2957, 2931, 2865, 1751 (C=O), 1731 (C=O). ^{1}H NMR ($CDCl_3$, 400 MHz) *δ* 5.14-5.19 (m, 1H), 4.84-4.90 (m, 1H), 2.51 (s, 1H), 2.15 (s, 3H), 1.71-1.84 (m, 4H), 1.34-1.47 (m, 4H), 1.25-1.31 (m, 8H), 0.84-0.88 (t, 6H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) *δ* 205.2, 204.7, 154.0, 82.1, 81.9, 80.24, 80.15, 74.7, 74.6, 68.4, 68.3, 34.4, 31.2, 31.1, 30.4, 25.8, 24.5, 24.4, 24.3, 22.34, 22.28, 13.84 ppm. GC-MS (EI, 70 eV) *m/z* (%) = 127.13 (5.82), 109.13 (19.25), 97.19 (6.90), 95 (12.29), 93.19 (7.96), 91.12 (7.8), 81.15 (36.26), 79.18 (28.14), 67.22 (100), 55.25 (22.65), 43.15 (61.30). HRMS (ESI): $C_{17}H_{29}O_4$ for $[M+H]^+$ calculated 297.2060, found 297.2062.



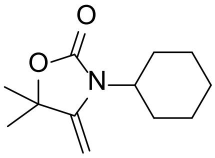
4a

Orange oil. IR (KBr): *ν*/cm^{-1} 2956, 2925, 2855, 1774 (C=O), 1677, 1640, 1618. ^{1}H NMR ($CDCl_3$, 400 MHz) *δ* 4.08 (d, *J* = 4.0 Hz, 1H), 3.98 (d, *J* = 4.0 Hz, 1H), 3.41 (t, *J* = 8.0 Hz, 2H), 1.66-1.59 (m, 2H), 1.49 (s, 6H), 0.94 (t, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) *δ* 155.7 (C=O), 150.9, 81.9, 79.0, 42.8, 27.9, 19.6, 11.0 ppm. GC-MS (EI, 70 eV) *m/z* (%) = 169.20 (M^+, 31.42), 128.15 (100), 96.15 (34.58), 84.10 (55.62), 68.10 (33.42). HRMS (ESI): $C_9H_{16}NO_2$ for $[M+H]^+$ calculated 170.1176, found 170.1173.



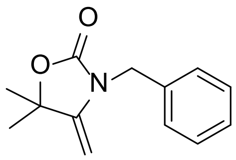
4b

Orange oil. ^{1}H NMR ($CDCl_3$, 400 MHz) *δ* 4.06 (d, *J* = 4.0 Hz, 1H), 3.97 (d, *J* = 4.0 Hz, 1H), 3.42 (t, *J* = 8.0 Hz, 2H), 1.61-1.53 (m, 2H), 1.48 (s, 6H), 1.37-1.28 (m, 2H), 0.92 (t, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) *δ* 155.6 (C=O), 150.9, 81.9, 79.0, 41.1, 28.3, 27.9, 19.9, 13.7 ppm. GC-MS (EI, 70 eV) *m/z* (%) = 183 (M^+, 21), 168 (84), 128 (32), 97 (58), 96 (100), 84 (52), 82 (84).



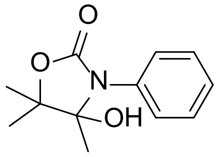
4c

White solid. M.p. 54-56 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) *δ* 4.19 (d, *J* = 4.0 Hz, 1H), 3.97 (d, *J* = 4.0 Hz, 1H), 3.58-3.50 (m, 1H), 2.11-2.01 (m, 2H), 1.86-1.64 (m, 4H), 1.45 (s, 6H), 1.32-1.14 (m, 4H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) *δ* 155.0 (C = O), 150.7, 81.1, 79.7, 53.7, 28.3, 27.9, 25.9, 25.1 ppm. GC-MS (EI, 70 eV) *m/z* (%) = 209.20 (10.35), 194.20 (2.67), 129.15 (7.80), 128.20 (100), 127.20 (24.77), 85.15 (3.98), 84.15 (31.08), 83.15 (4.94), 68.10 (8.82), 67.10 (15.89).



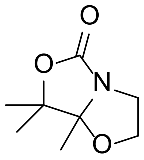
4d

Orange-yellow oil. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.33-7.25 (m, 5H, Ar-H), 4.64 (s, 2H), 4.03 (d, J = 4.0 Hz, 1H), 3.96 (d, J = 2.4 Hz, 1H), 1.51 (s, 6H) ppm. ^{13}C NMR (100.6 MHz, CDCl$_3$) δ 155.8, 150.2, 135.2, 128.6, 127.6, 126.9, 82.2, 80.5, 45.0, 27.8 ppm. GC-MS (EI, 70 eV) *m/z* (%) = 217.15 (M$^+$, 21.11), 172.20 (6.93), 91.10 (100).



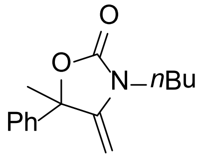
4e

Straw yellow solid. M.p. 131-133 °C. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.39-7.28 (m, 5H, Ar), 4.82 (1H, OH), 1.40 (s, 3H), 1.33 (s, 3H), 1.25 (s, 3H) ppm. ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 156.5, 134.8, 128.8, 127.6, 127.4, 91.7, 86.2, 25.1, 20.1 ppm. GC-MS (EI, 70 eV) *m/z* (%) = 221.15 (10.90), 179.15 (7.58), 178.15 (14.11), 137.10 (5.94), 120.10 (14.28), 119.10 (100), 94.10 (3.65), 93.10 (43.08), 92.10 (12.76), 91.10 (53.70), 77.10 (13.95), 66.10 (6.31), 65.10 (18.56), 64.10 (35.03), 63.10 (14.27).



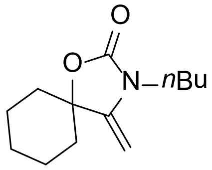
4f

Straw yellow solid. M.p. 67-69 °C. IR (KBr): ν/cm^{-1} 3474, 3414, 2928, 1751 (C=O), 1449, 1408, 1341, 1288, 1206, 1093. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 4.07-4.02 (m, 1H), 3.92-3.80 (m, 2H), 3.35-3.28 (m, 1H), 1.45 (s, 6H), 1.32 (s, 3H) ppm. ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 161.6 (C = O), 100.3, 84.5, 63.6, 45.4, 25.5, 20.9, 17.5 ppm. GC-MS (EI, 70 eV) *m/z* (%) = 171.20 (9.08), 129.20 (6.94), 128.20 (100), 127.20 (4.96), 96.15 (23.79), 85.15 (9.88), 84.15 (49.07), 82.15 (10.53), 81.15 (7.86), 69.10 (7.31), 68.10 (24.51), 67.10 (17.85). HRMS (ESI): $C_8H_{14}NO_3$ for [M+H]$^+$ calculated 172.0968, found 172.0968.



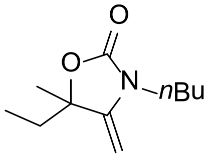
4g

Yellow oil. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.47-7.32 (m, 5H, Ar-H), 4.23 (1H), 4.10 (1H), 3.53-3.46 (m, 2H), 1.87 (s, 3H), 1.61-1.58 (m, 2H), 1.34-1.26 (m, 2H), 0.93 (t, 3H) ppm. ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 155.5, 149.7, 141.2, 128.5, 128.3, 124.8, 84.2, 81.9, 41.3, 28.3, 27.5, 19.8, 13.6 ppm. GC-MS (EI, 70 eV) *m/z* (%) = 245.20 (M$^+$, 14.00), 159.15 (45.39), 158.20 (80.47), 147.15 (34.51), 146.20 (39.75), 144.20 (93.03), 131.15 (23.28), 130.15 (25.26), 129.15 (31.43), 118.15 (36.85), 117.15 (32.89), 103.10 (45.28), 97.15 (100), 77.10 (29.86).



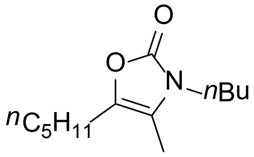
4h

White solid. M.p. 60-62 °C. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 4.04 (d, J = 4.0 Hz, 1H), 3.92 (d, 1H), 3.40 (t, J = 8.0 Hz, 2H), 1.83-1.30 (m, 14H), 0.90 (t, 3H) ppm. ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 155.8 (C=O), 150.8, 83.5, 79.2, 40.9, 36.8, 28.3, 24.6, 21.5, 19.8, 13.6 ppm. GC-MS (EI, 70 eV) *m/z* (%) = 223.20 (31.73), 181.20 (49.51), 168.20 (100), 137.20 (29.15), 136.20 (23.85), 112.10 (51.27), 95.15 (25.85), 67.10 (20.20).



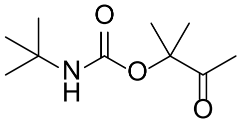
4i

Colourless oil. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 4.11 (d, J = 4.0 Hz, 1H), 3.92 (d, J = 4.0 Hz, 1H), 3.50-3.35 (m, 2H), 1.86-1.77 (m, 1H), 1.69-1.60 (m, 1H), 1.61-1.53 (m, 2H), 1.45 (s, 3H), 1.38-1.29 (m, 2H), 0.93 (t, 3H), 0.87 (t, 3H) ppm. ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 156.0, 149.3, 84.6, 79.2, 41.1, 33.6, 28.3, 26.6, 19.9, 13.7, 7.3 ppm. GC-MS (EI, 70 eV) *m/z* (%) = 199.15 (5.97), 171.15 (15.83), 144.15 (100), 98.10 (11.93), 84.10 (22.83), 83.10 (22.54), 82.10 (46.32).



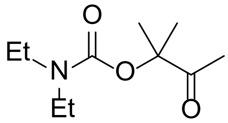
4j

Yellow oil. IR (KBr): *ν*/cm^{-1} 2957, 2930, 2866, 1739 (C=O). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 3.45 (t, 2H), 2.30 (t, 2H), 1.92 (s, 3H), 1.49-1.58 (m, 4H), 1.22-1.33 (m, 6H), 0.84-0.93 (m, 6H) ppm. ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 155.8, 135.3, 117.0, 41.5, 31.3, 31.0, 27.2, 24.3, 22.3, 19.8, 13.9, 13.6, 7.9 ppm. GC-MS (EI, 70 eV) *m/z* (%) = 225.20 (M$^+$, 17.88), 168.20 (100), 112.10 (81.52). HRMS (ESI): $C_{13}H_{24}NO_2$ for [M+H]$^+$ calculated 226.1802, found 226.1804.



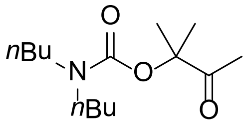
4k

White solid. M.p. 78-79 °C. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 4.77 (1H, NH), 2.12 (s, 3H), 1.39 (s, 6H), 1.29 (s, 9H) ppm. ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 208.0 (C=O), 153.6 (N-C=O), 82.3, 50.5, 28.8, 23.5, 23.3 ppm. GC-MS (EI, 70 eV) *m/z* (%) = 202.30 [(M+H)$^+$, 1.02], 201.30 (M$^+$, 0.11), 186.20 [(M-CH$_3$)$^+$, 3.21], 158.20 [(M-CH$_3$CO)$^+$, 100], 115.20 (88.33), 102.15 (24.62), 85.15 (25.06), 84.10 (69.08), 60.10 (20.19).



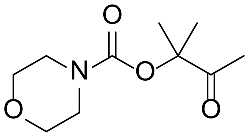
6a

Straw yellow oil. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 3.30-3.25 (q, 4H, CH$_2$), 2.12 (s, 3H), 1.45 (s, 6H), 1.14 (m, 6H) ppm. ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 207.7, 154.6, 82.8, 41.8, 41.6, 23.6, 23.4, 14.1, 13.5 ppm. GC-MS (EI, 70 eV) *m/z* (%) = 202.15 (0.26), 159.20 (1.72), 158.20 (16.15), 102.15 (3.34), 101.15 (6.35), 100.20 (100), 72.10 (46.64).



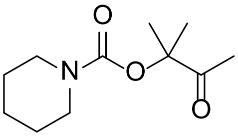
6b

Yellow oil. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 3.20 (t, 4H), 2.11 (s, 3H), 1.52-1.47 (m, 4H), 1.43 (s, 6H), 1.34-1.24 (m, 4H), 0.92 (6H) ppm. ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 207.7 (C=O), 155.0 (N-C=O), 82.8, 47.0, 46.7, 30.8, 30.1, 23.6, 23.3, 19.9, 13.8 ppm. GC-MS (EI, 70 eV) *m/z* (%) = 258.25 (0.46), 215.20 (1.63), 214.20 (11.61), 173.20 (1.24), 172.20 (11.62), 157.20 (10.32), 156.20 (100), 101.15 (2.14), 100.15 (35.17), 88.10 (6.78), 87.15 (1.69), 86.15 (27.01), 85.10 (13.69).



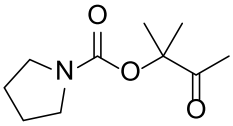
6c

Orange solid. M.p. 75-77 °C ^{1}H NMR (CDCl$_3$, 400 MHz) δ 3.62 (t, J = 4.0 Hz, 4H), 3.43 (t, J = 20.0 Hz, 4H), 2.09 (s, 3H), 1.42 (s, 6H) ppm. ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 207.2, 154.0, 83.3, 66.5, 44.5, 43.6, 23.5, 23.5 ppm. GC-MS (EI, 70 eV) *m/z* (%) = 215.10 (1.46), 173.15 (1.96), 172.15 (18.30), 115.15 (6.22), 114.15 (100), 71.10 (2.10), 70.10 (48.56), 69.10 (1.69).



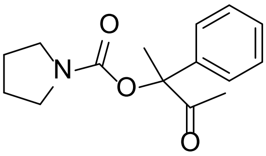
6d

Pale brown oil. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 3.39 (m, 4H), 2.11 (s, 3H), 1.59-1.49 (m, 6H), 1.43 (s, 6H) ppm. ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 207.5, 154.0, 82.7, 44.6, 25.6, 24.0, 23.4, 23.2 ppm. GC-MS (EI, 70 eV) *m/z* (%) = 213.15 (0.33), 171.15 (1.66), 170.20 (15.03), 129.15 (1.20), 128.15 (12.49), 114.15 (1.02), 113.15 (8.01), 112.15 (100), 69.10 (45.97).



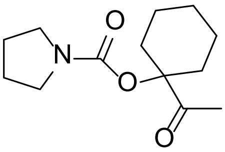
6e

Colourless oil. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 3.37 (m, 4H), 2.14 (s, 3H), 1.87 (m, 4H), 1.45 (s, 6H) ppm. ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 208.0, 153.8, 62.8, 46.0, 23.8, 23.6 ppm. GC-MS (EI, 70 eV) *m/z* (%) = 199.15 (0.49), 157.15 (2.07), 156.20 (18.73), 100.15 (0.51), 99.15 (7.78), 98.15 (100).



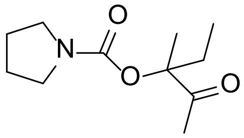
6f

White solid. M.p. 126-127 °C. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.46-7.43 (m, 2H), 7.37-7.27 (m, 3H), 3.68-3.56 (m, 2H), 3.45-3.52 (t, 2H), 1.97 (s, 3H), 1.85 (s, 3H) ppm. ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 204.5, 153.2, 139.6, 128.6, 127.8, 124.7, 86.7, 46.2, 25.7, 24.9, 23.8, 23.6 ppm. GC-MS (EI, 70 eV) *m/z* (%) = 219.15 (18.69), 218.15 (11.05), 160.15 (5.98), 105.10 (23.48), 98.10 (100).



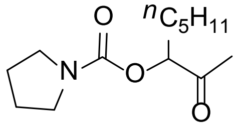
6g

Colourless solid. M.p. 62-63 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.45 (2H), 3.36 (2H), 2.12 (3H), 2.06-2.03 (2H), 1.89 (4H), 1.67-1.57 (5H), 1.54-1.44 (2H), 1.23 (1H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 208.3 (C=O), 153.4 (N-C=O), 84.0, 46.0, 45.9, 30.9, 25.6, 25.1, 24.8, 23.6, 21.3 ppm. GC-MS (EI, 70 eV) *m/z* (%) = 196.15 (M^+-43, 14.56), 98.15 (100).



6h

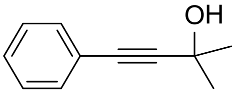
Straw yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.36 (4H), 2.13 (3H), 1.96-1.87 (5H), 1.72-1.63 (1H), 1.45 (s, 3H), 0.88 (t, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 208.3(C=O), 153.4 (N-C=O), 84.0, 46.0, 45.9, 30.9, 25.6, 25.1, 24.8, 23.6, 21.3 ppm. GC-MS (EI, 70 eV) *m/z* (%) = 170.15 (M^+-43, 16.68), 98.15 (100).



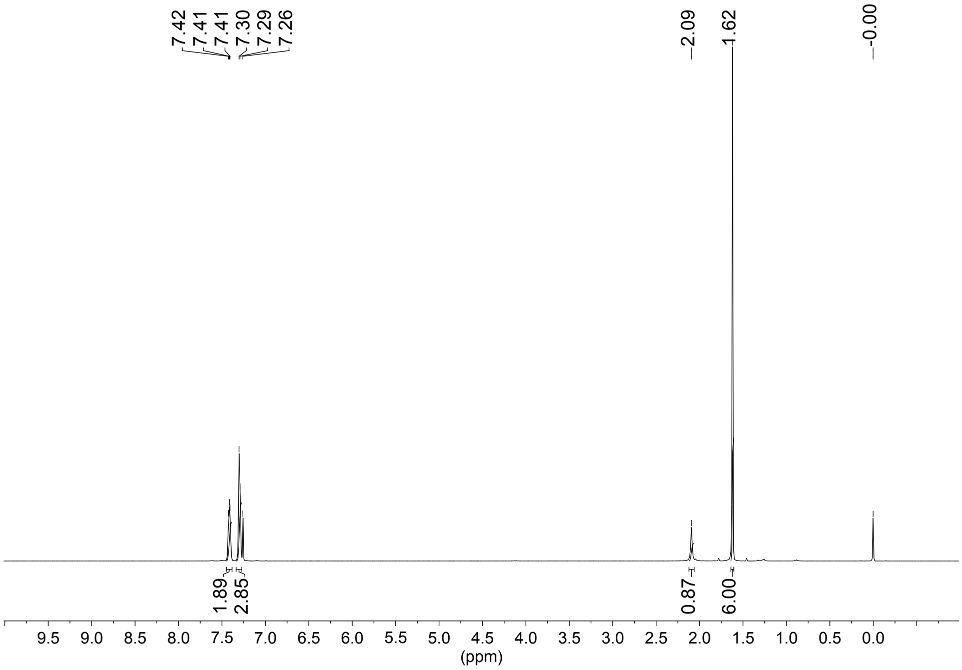
6i

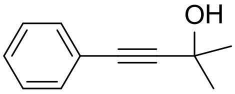
Straw yellow oil. IR (KBr): *ν*/cm^{-1} 2955, 2926, 2872, 1709 (C=O). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.89 (t, *J* = 4.0 Hz, 1H), 3.38-3.46 (4H), 2.15 (s, 3H), 1.67-1.88 (m, 6H), 1.29-1.40 (m, 6H), 0.87 (t, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 207.1, 154.3, 79.0, 46.2, 45.8, 31.4, 30.5, 26.1, 25.7, 24.9, 24.8, 22.3, 13.9 ppm. GC-MS (EI, 70 eV) *m/z* (%) = 198.15 (M^+-43, 4.35), 98.15 (100). HRMS (ESI): $C_{13}H_{24}NO_3$ for $[M+H]^+$ calculated 242.1751, found 242.1752.

3. NMR Spectral Copies of the Substrates and Products

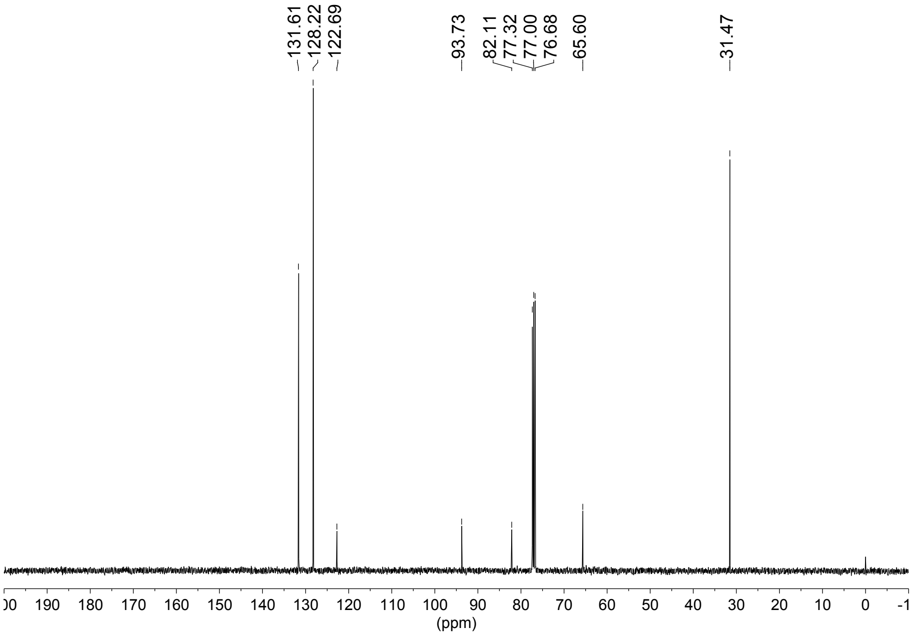


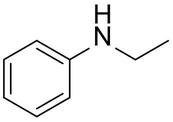
1h ^{1}H NMR ($CDCl_3$, 400 MHz)



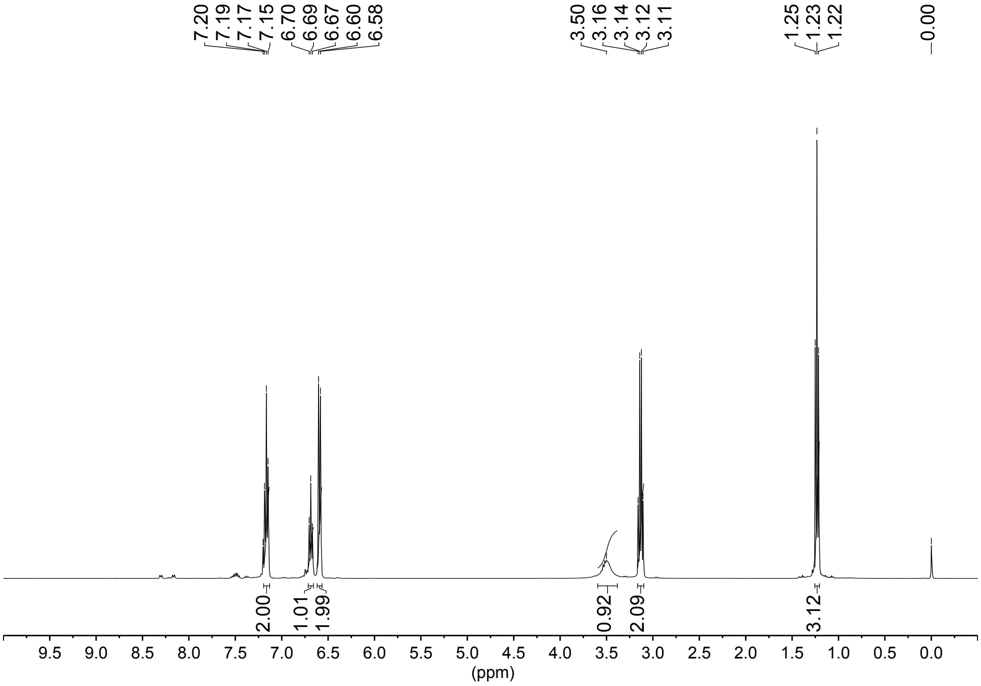


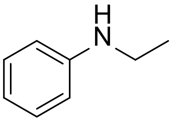
1h ^{13}C NMR ($CDCl_3$, 100.6 MHz)



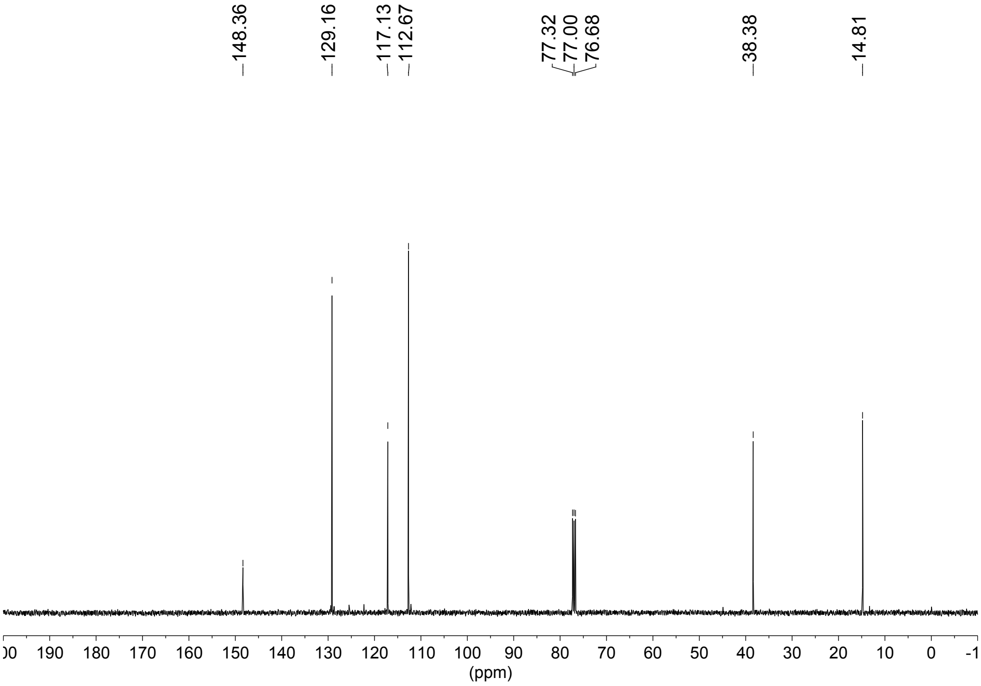


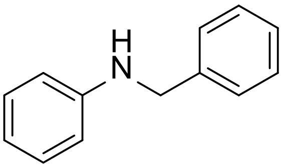
6j ^{1}H NMR ($CDCl_3$, 400 MHz)





6j ^{13}C NMR ($CDCl_3$, 100.6 MHz)





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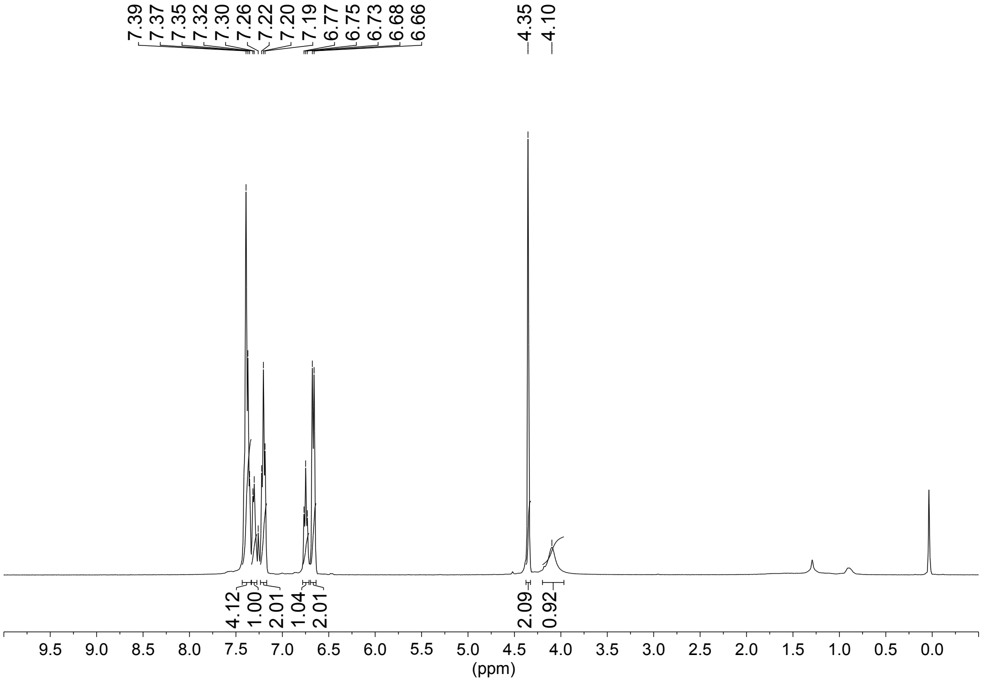
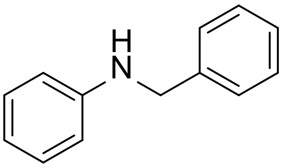
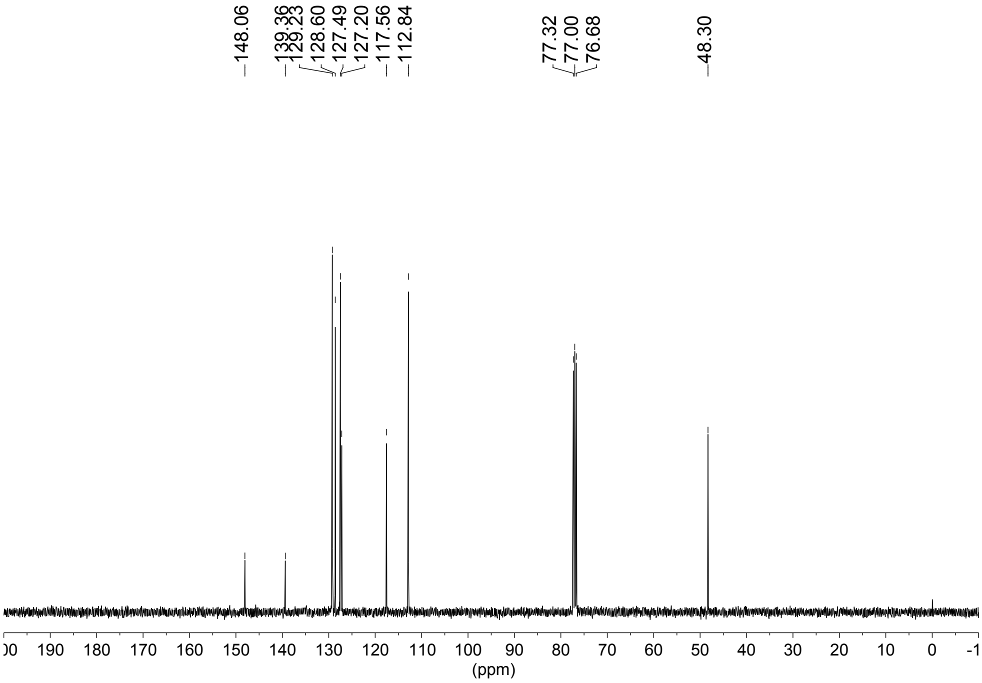
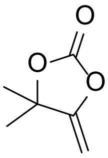


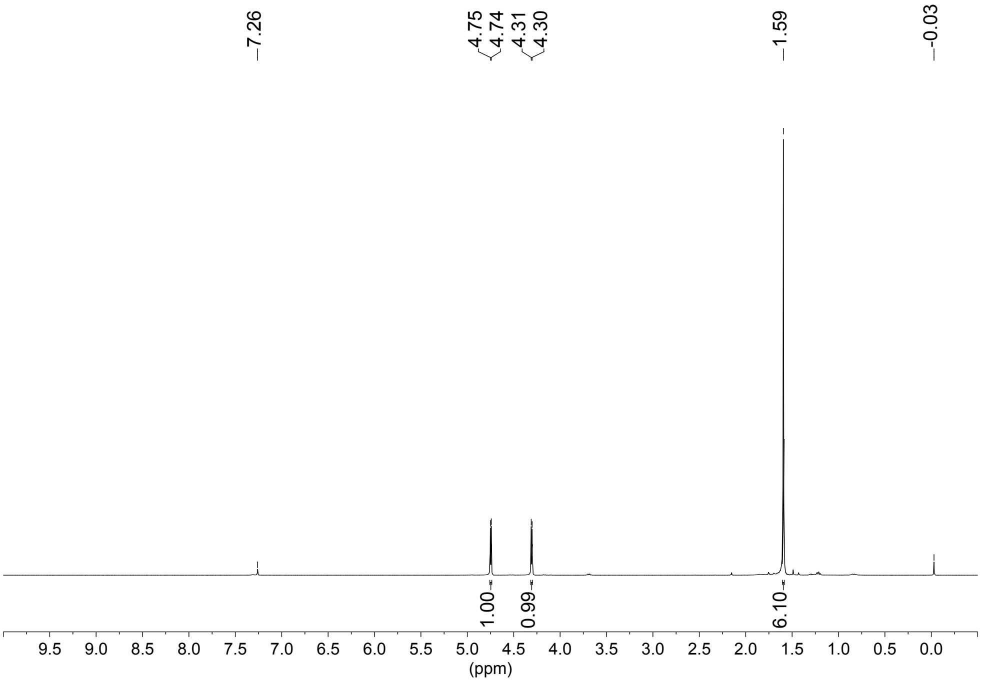


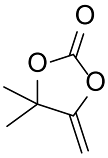
6k ^{13}C NMR ($CDCl_3$, 100.6 MHz)



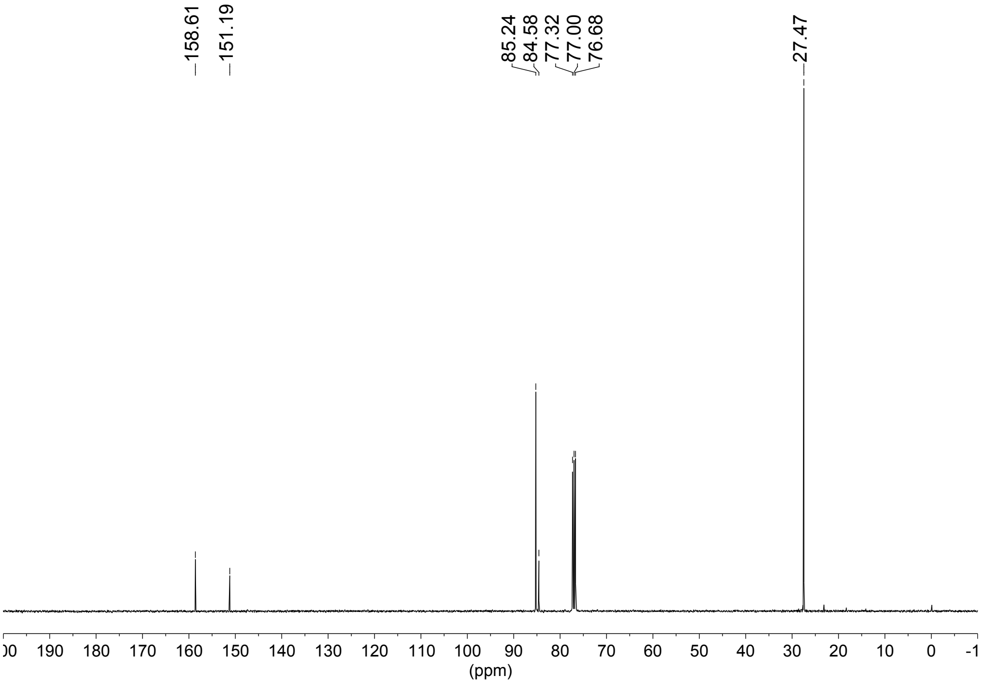


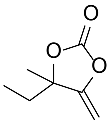
2a ^{1}H NMR ($CDCl_3$, 400 MHz)





2a ^{13}C NMR ($CDCl_3$, 100.6 MHz)





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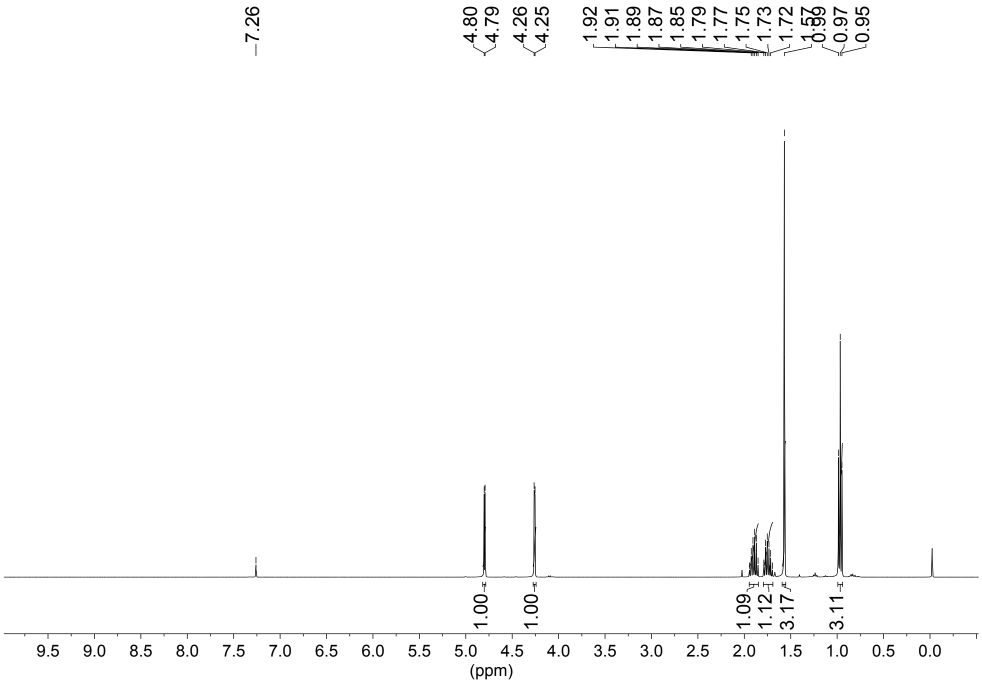
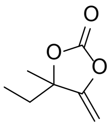
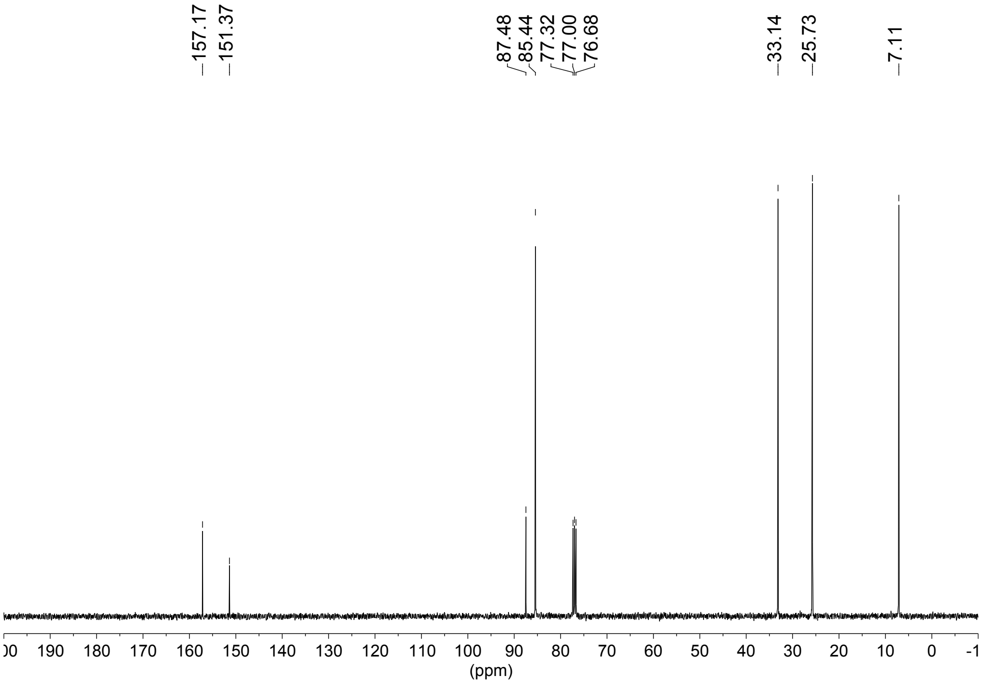
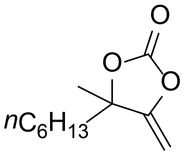


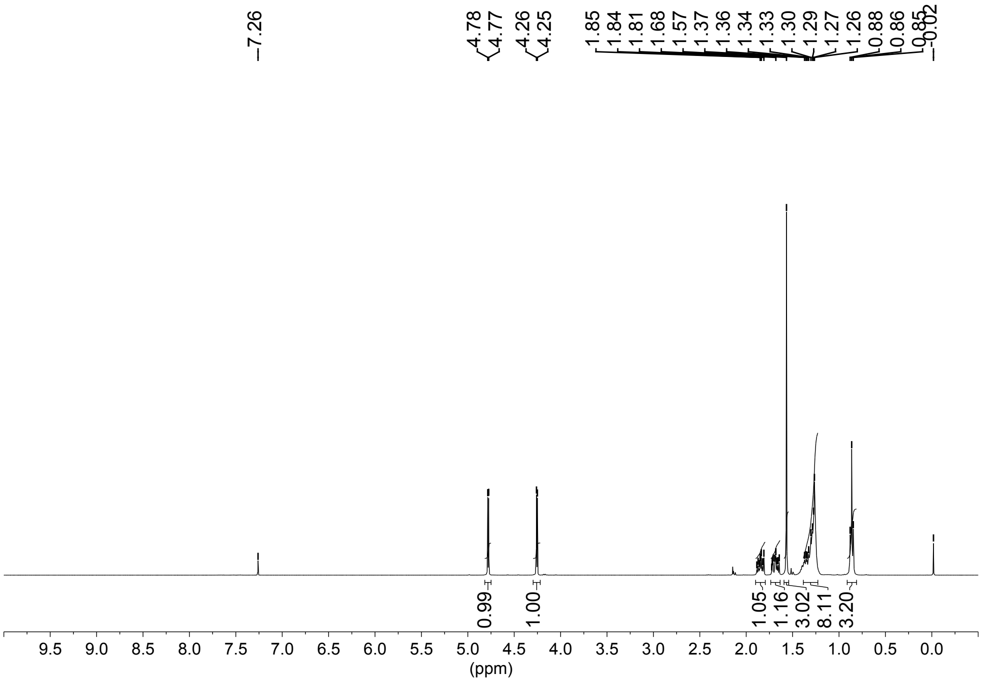


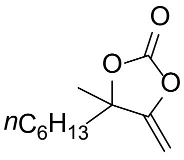
2b ^{13}C NMR (CDCl$_3$, 100.6 MHz)



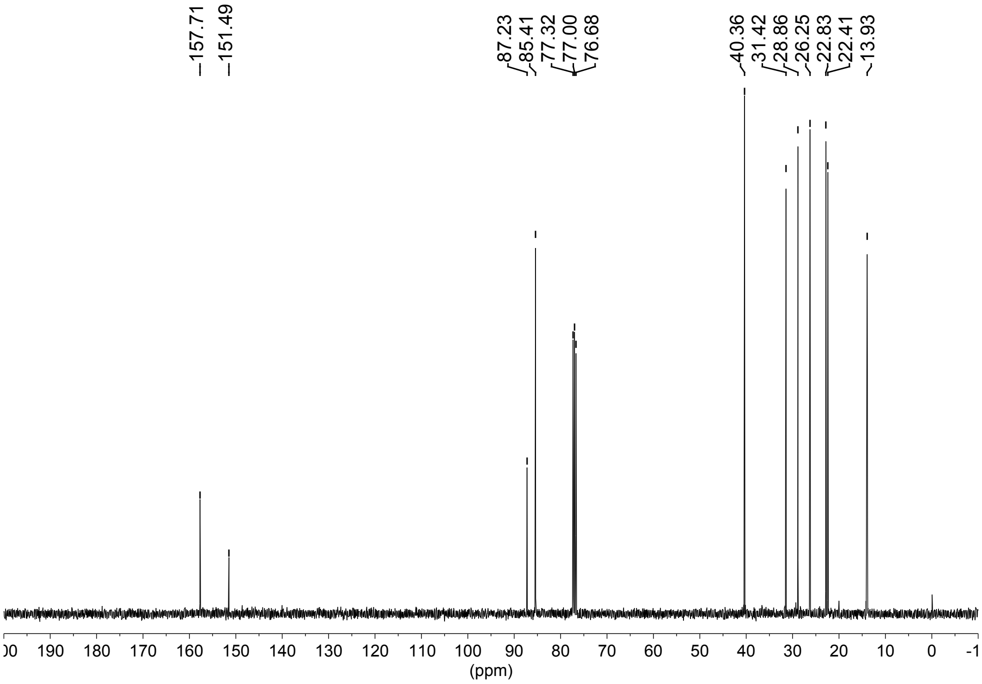


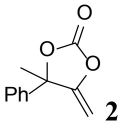
2c ^{1}H NMR ($CDCl_3$, 400 MHz)



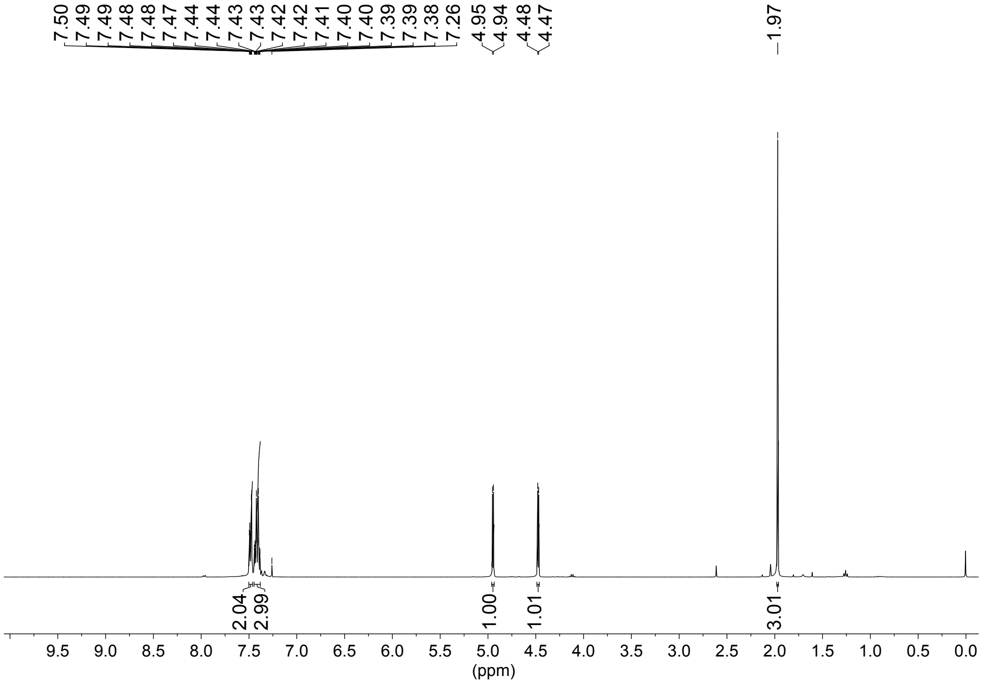


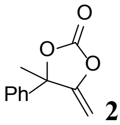
2c ^{13}C NMR ($CDCl_3$, 100.6 MHz)





2d ^{1}H NMR (CDCl$_3$, 400 MHz)





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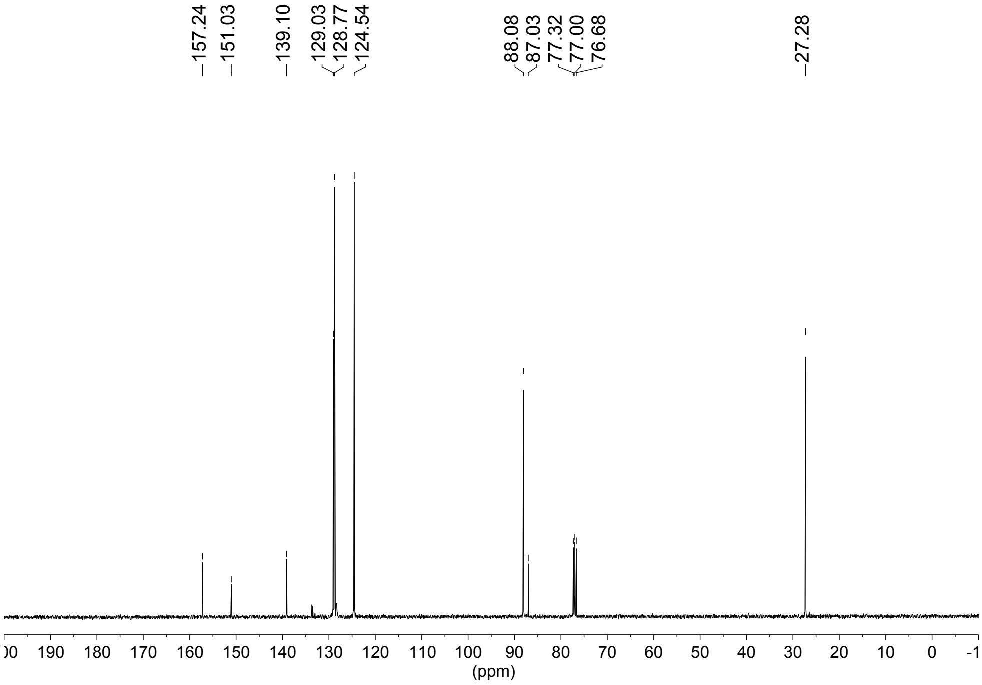
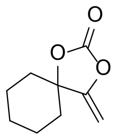
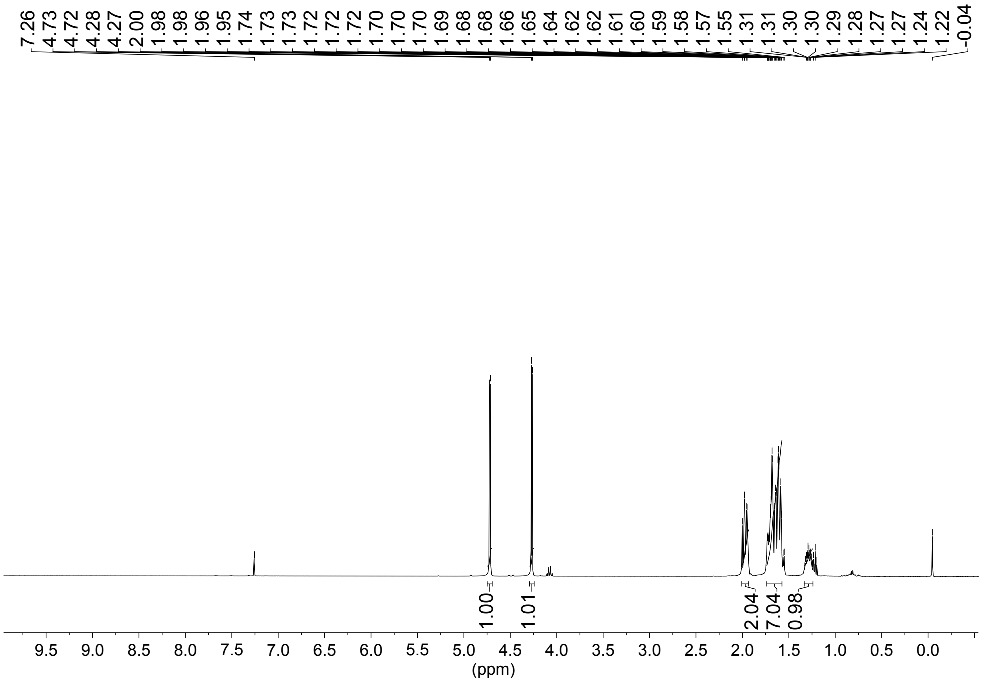
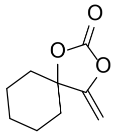


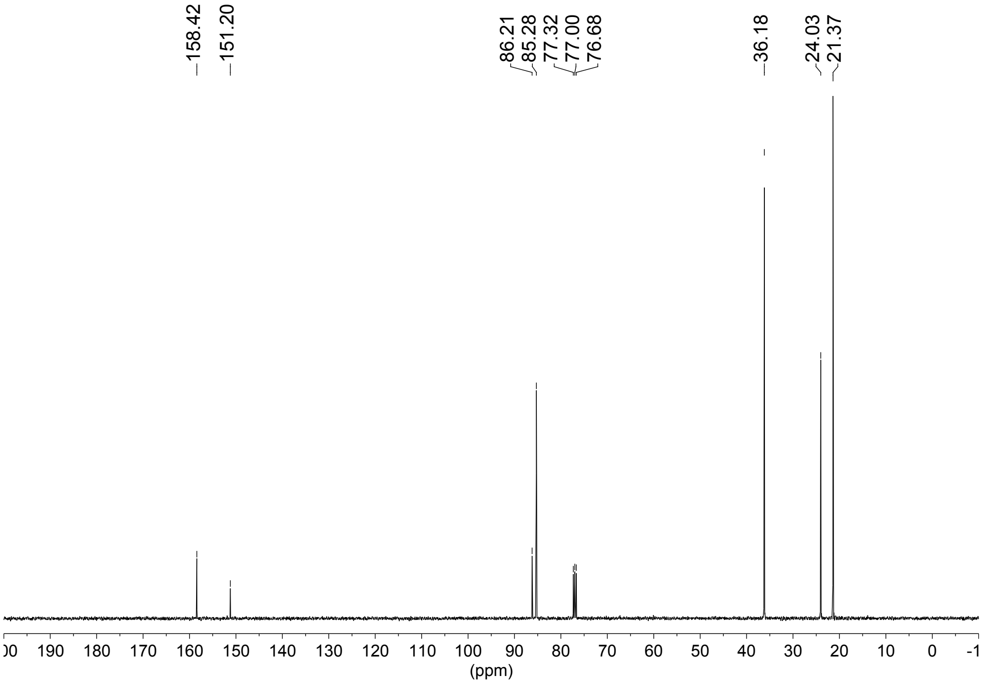


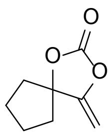
2e ^{1}H NMR ($CDCl_3$, 400 MHz)



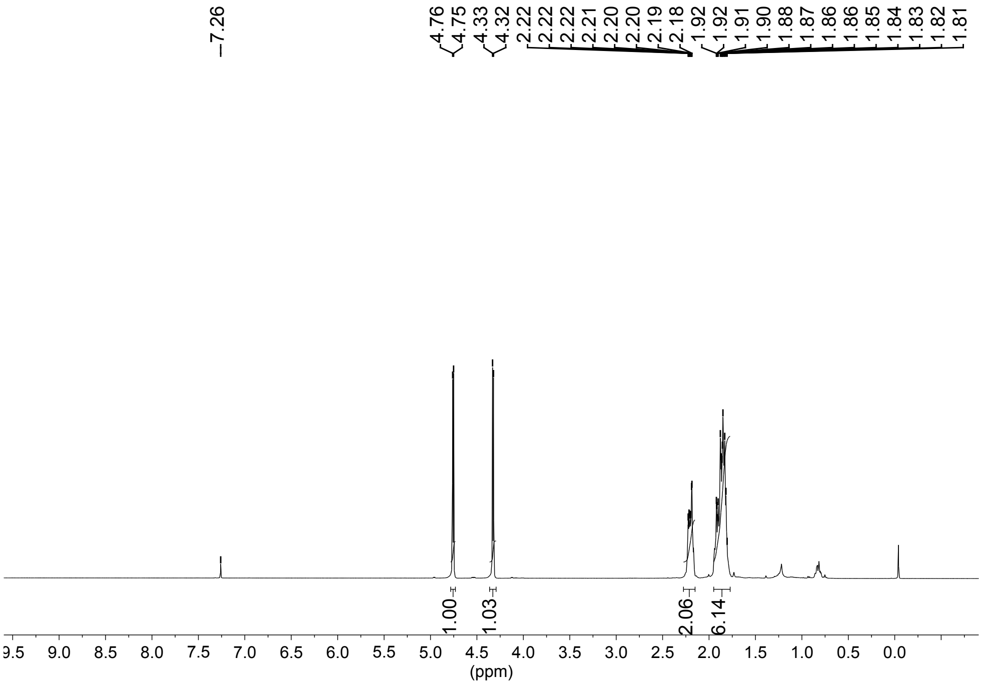


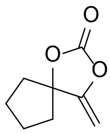
2e ^{13}C NMR ($CDCl_3$, 100.6 MHz)



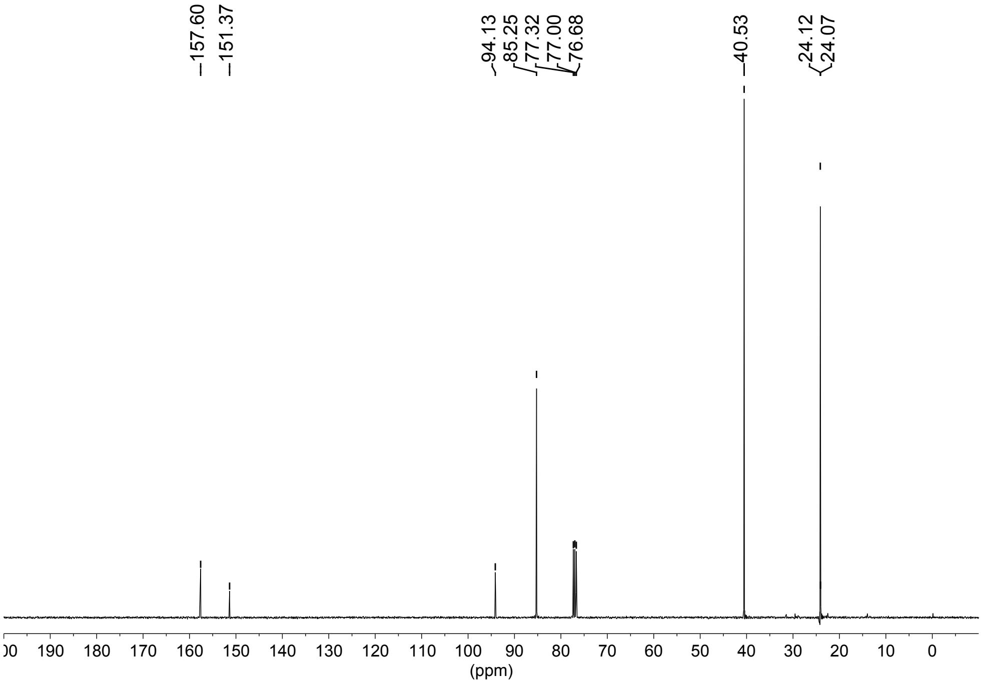


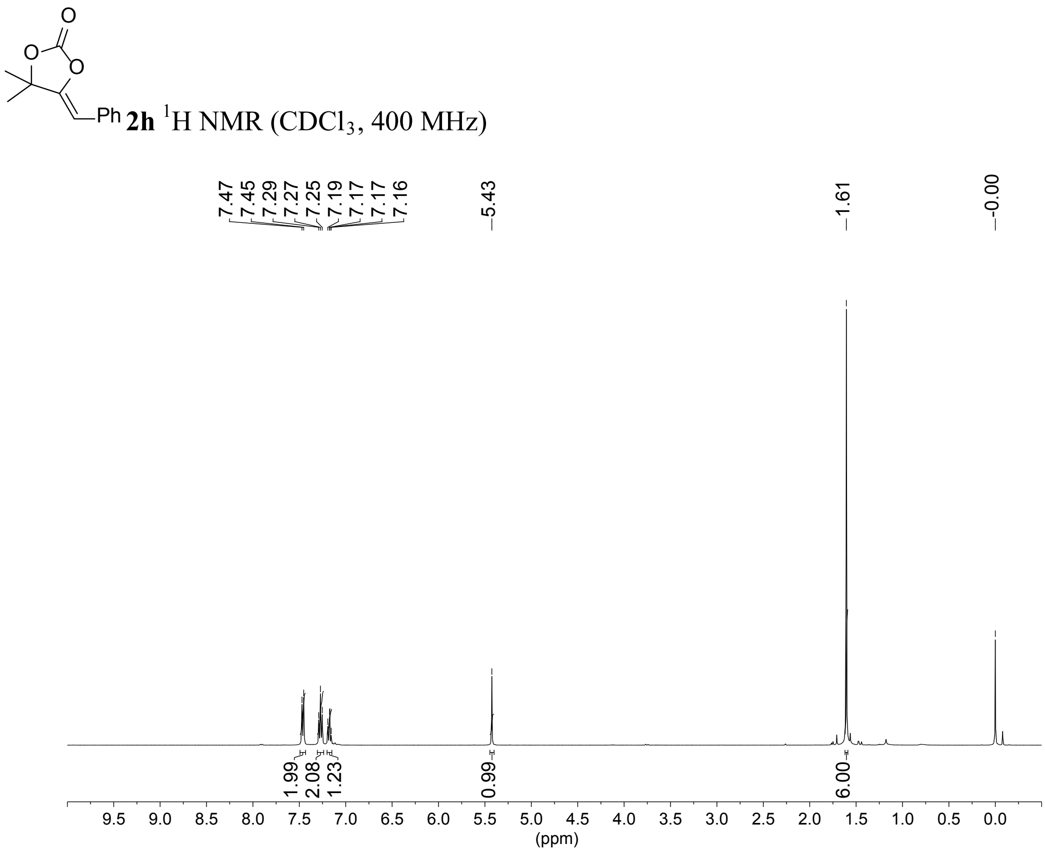
2g ^{1}H NMR ($CDCl_3$, 400 MHz)



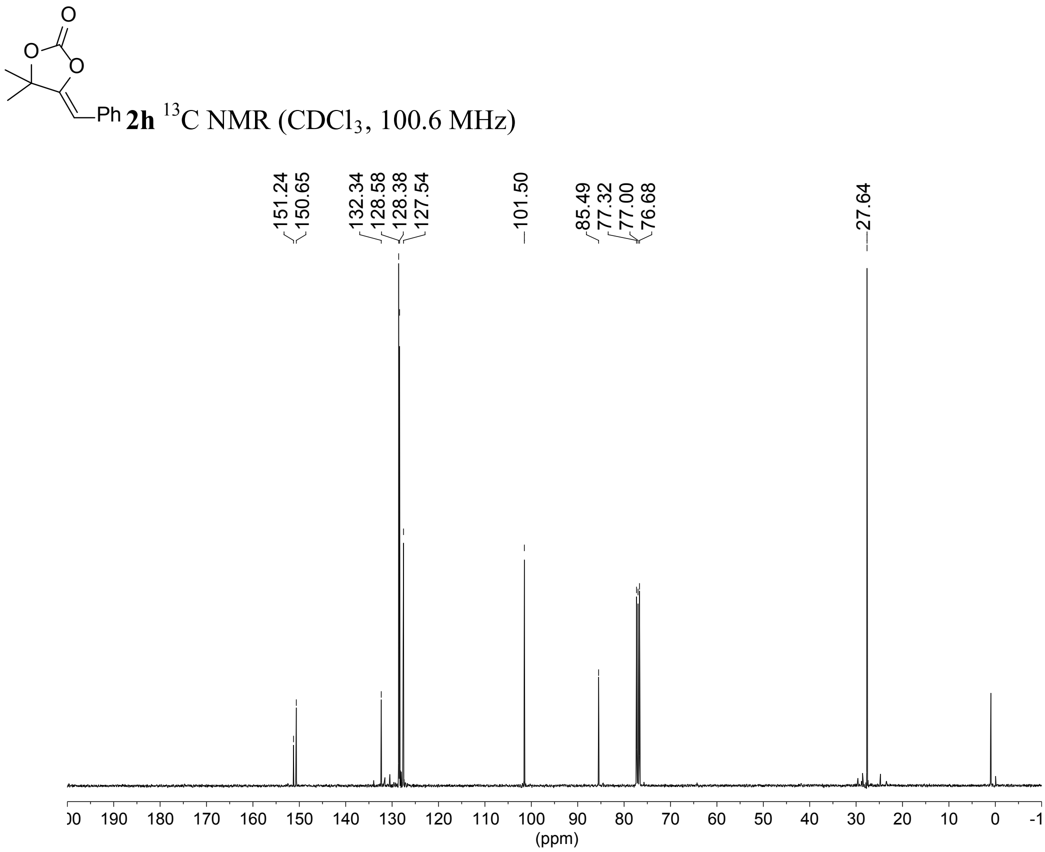


2g ^{13}C NMR ($CDCl_3$, 100.6 MHz)

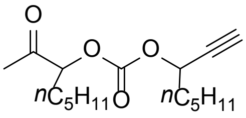




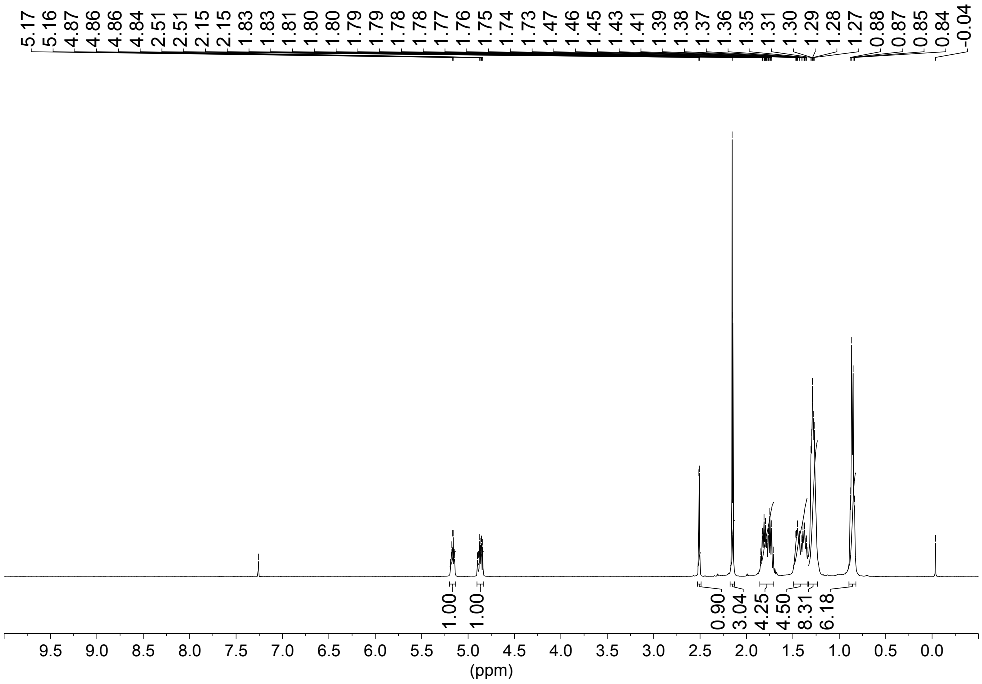
2h ^{1}H NMR ($CDCl_3$, 400 MHz)

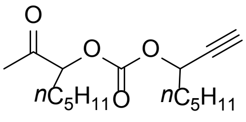


2h ^{13}C NMR ($CDCl_3$, 100.6 MHz)

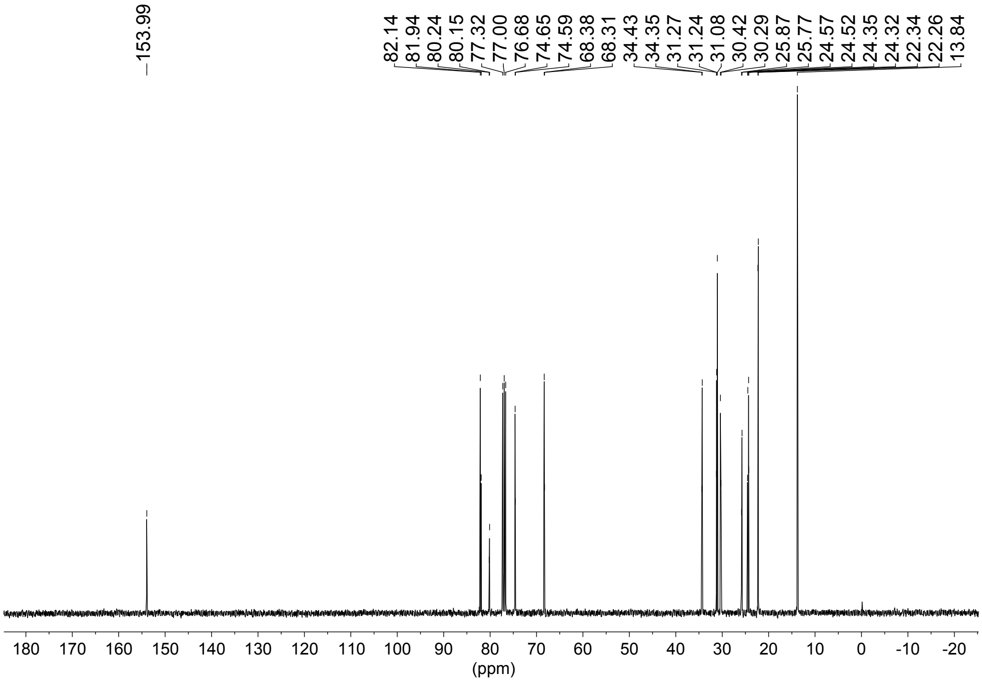


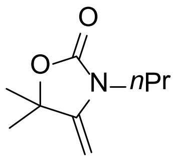
2i ^{1}H NMR ($CDCl_3$, 400 MHz)



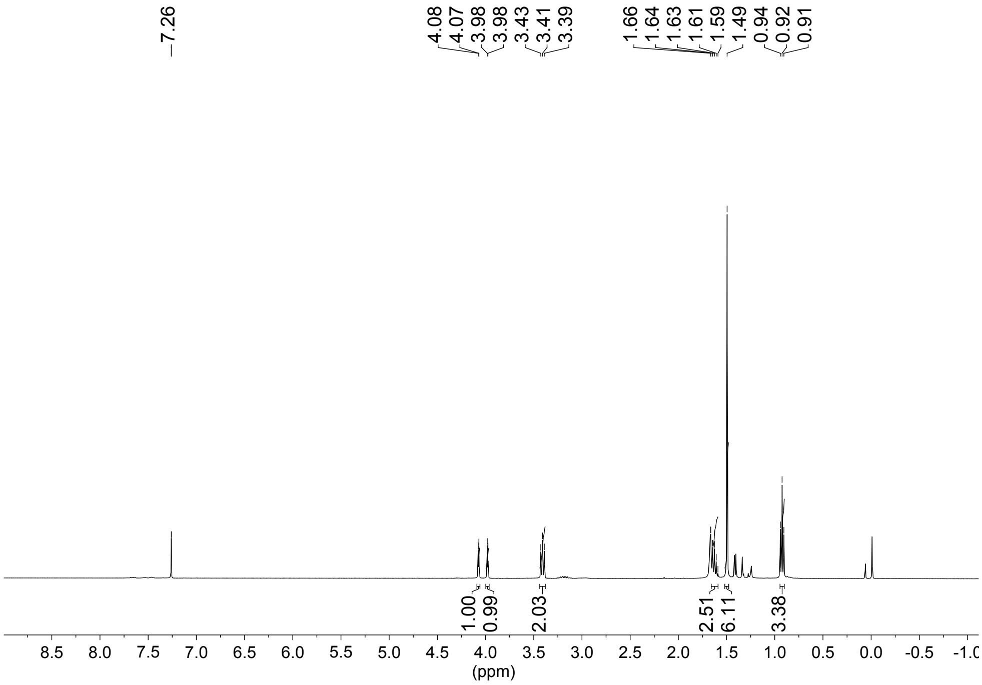


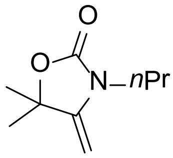
2i ^{13}C NMR ($CDCl_3$, 100.6 MHz)



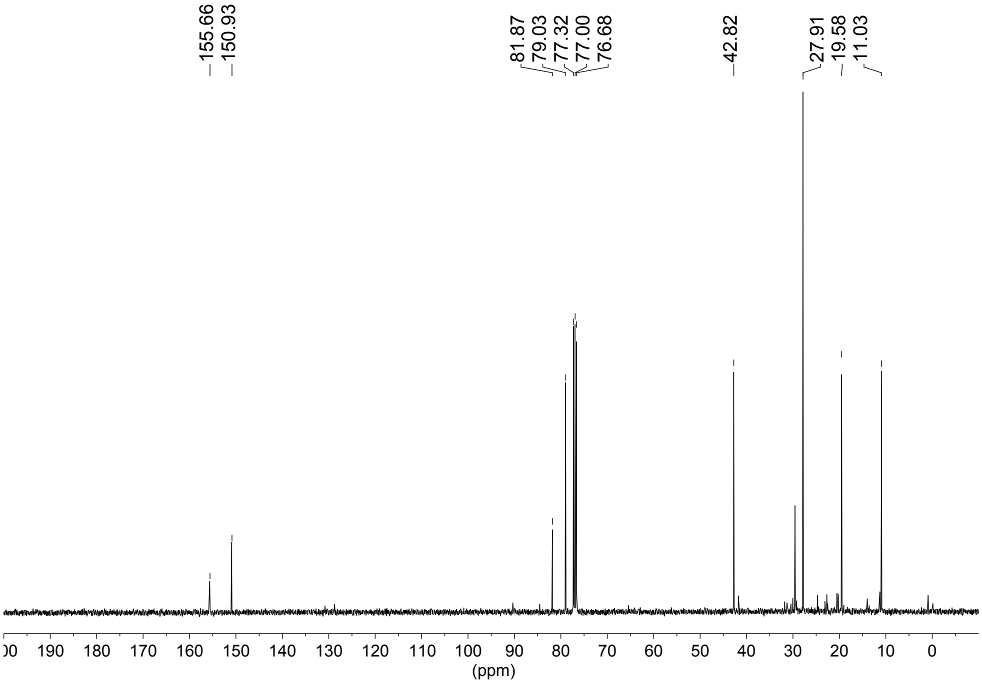


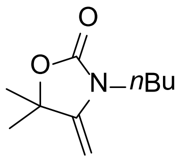
4a ^{1}H NMR (CDCl$_3$, 400 MHz)



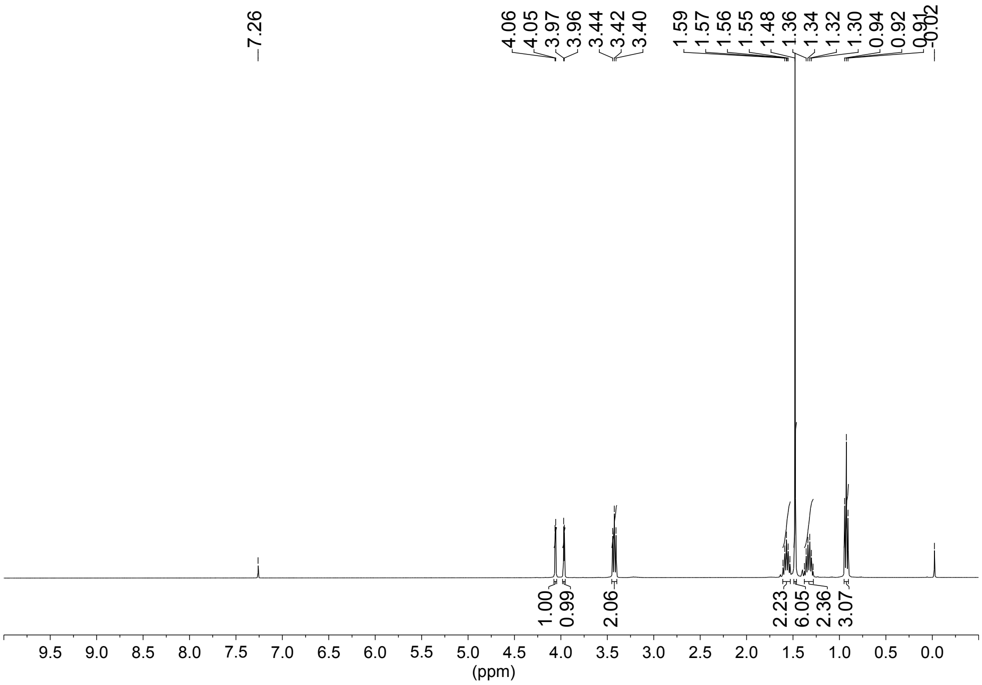


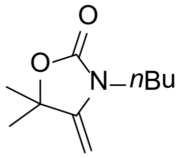
4a ^{13}C NMR (CDCl$_3$, 100.6 MHz)



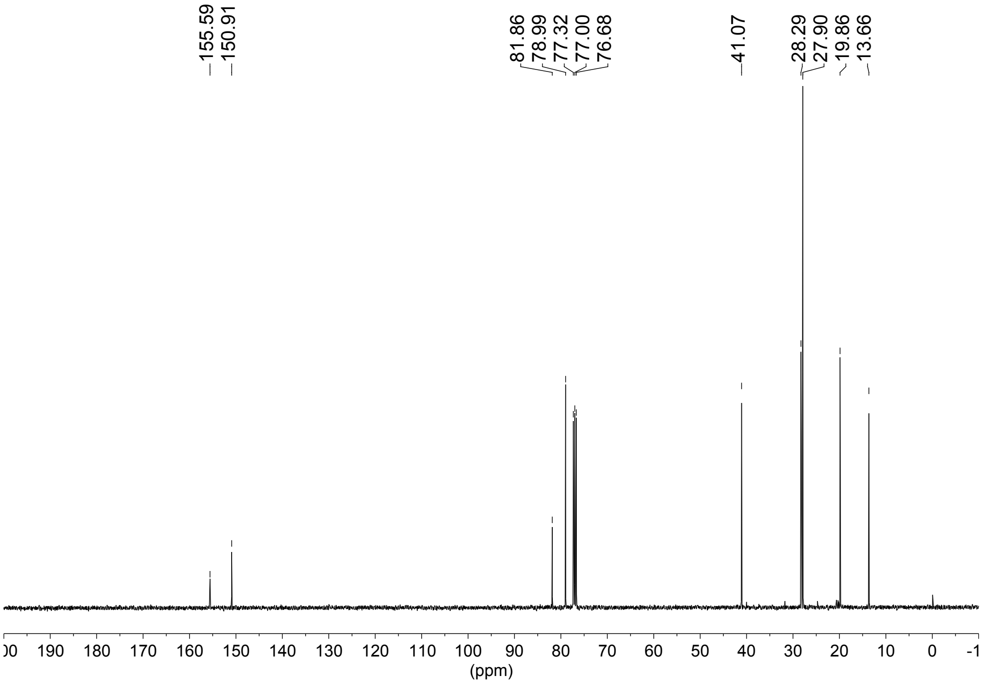


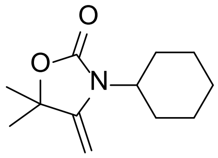
4b ^{1}H NMR (CDCl$_3$, 400 MHz)



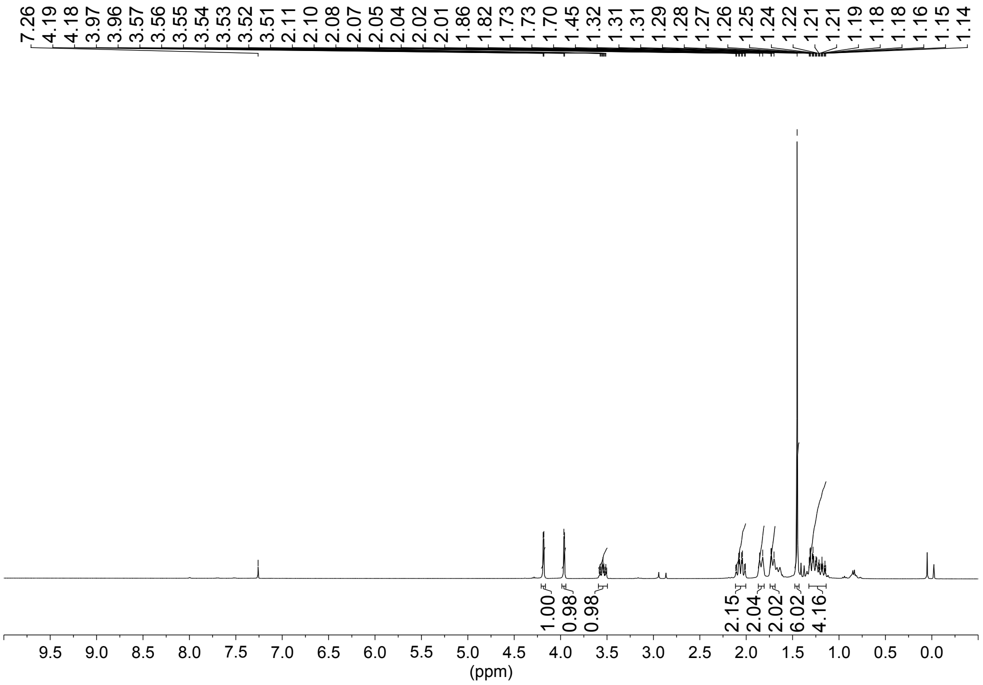


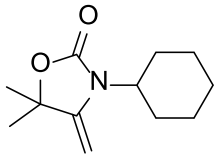
4b ^{13}C NMR (CDCl$_3$, 100.6 MHz)



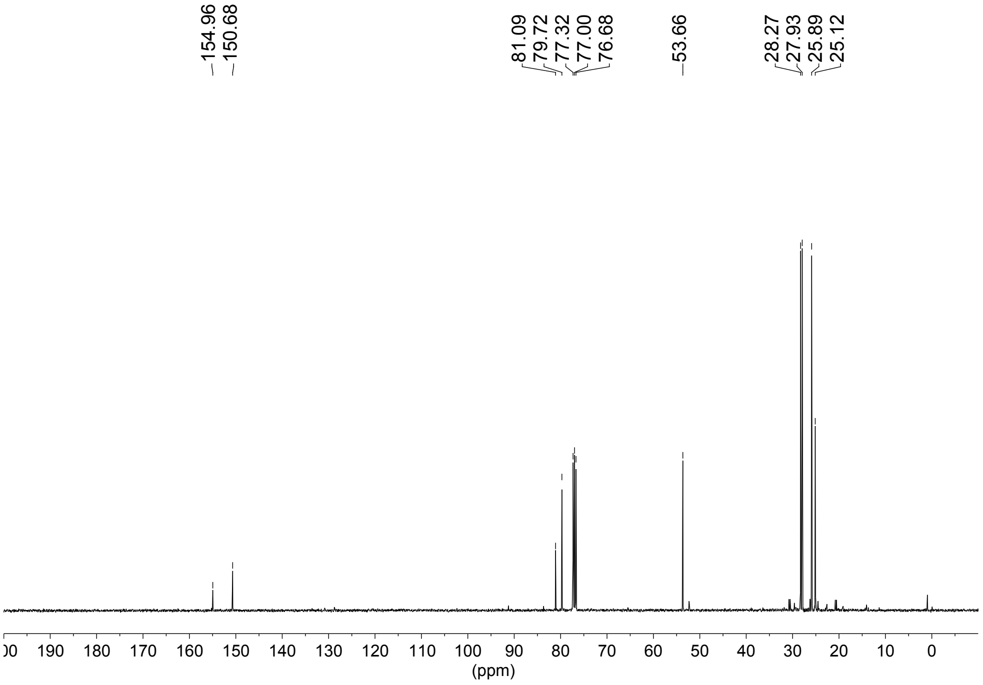


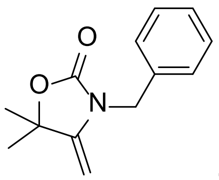
4c ^{1}H NMR (CDCl$_3$, 400 MHz)



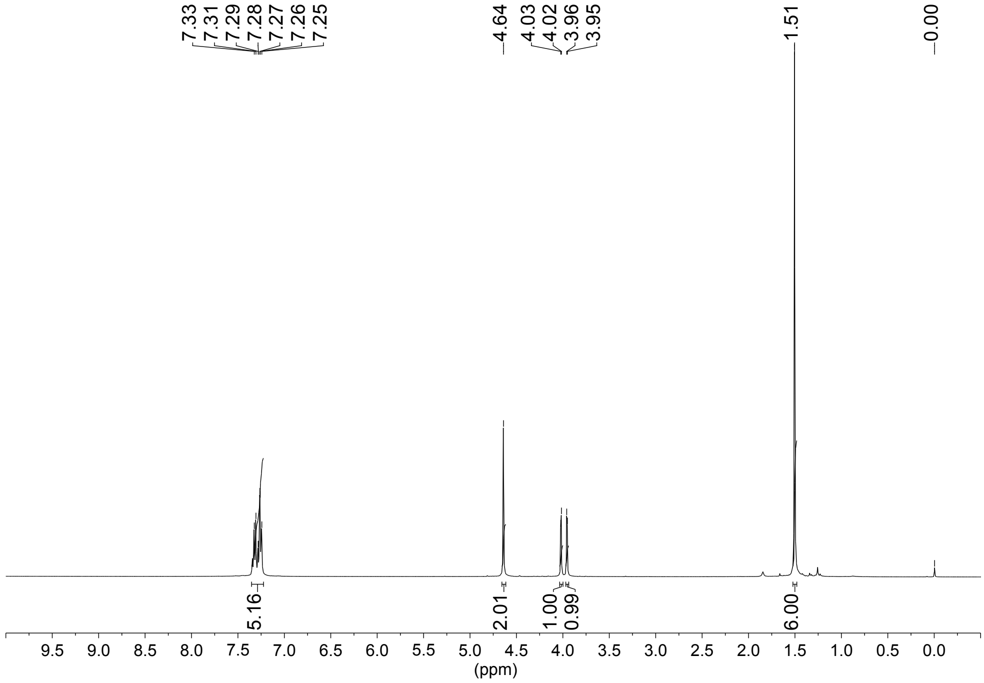


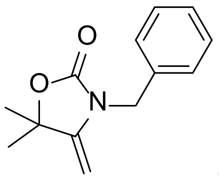
4c ^{13}C NMR (CDCl$_3$, 100.6 MHz)



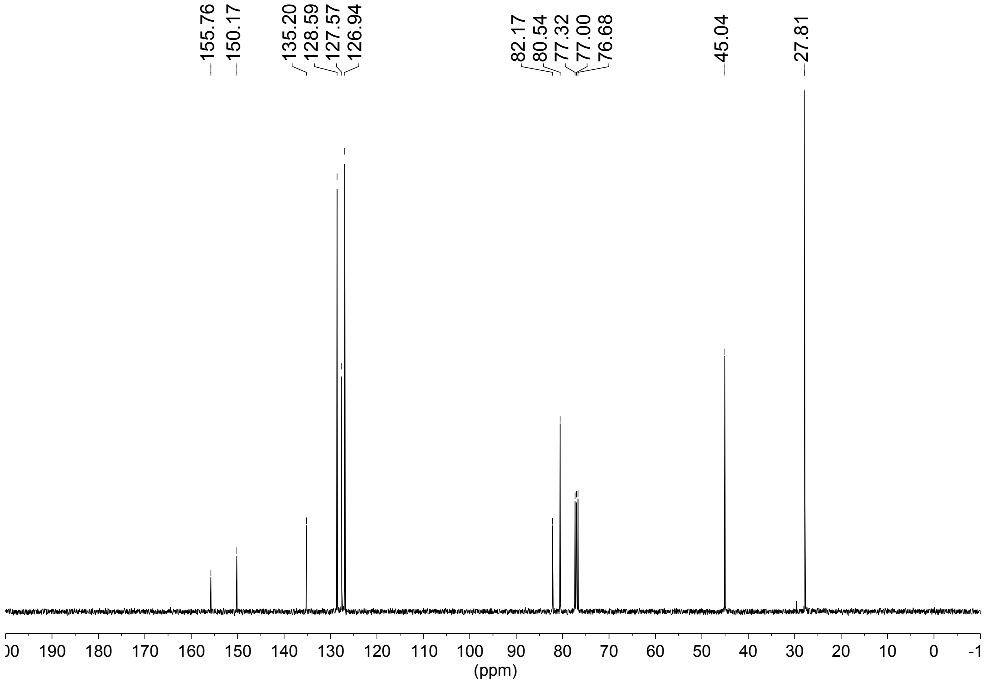


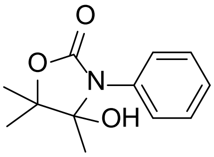
4d ^{1}H NMR ($CDCl_3$, 400 MHz)



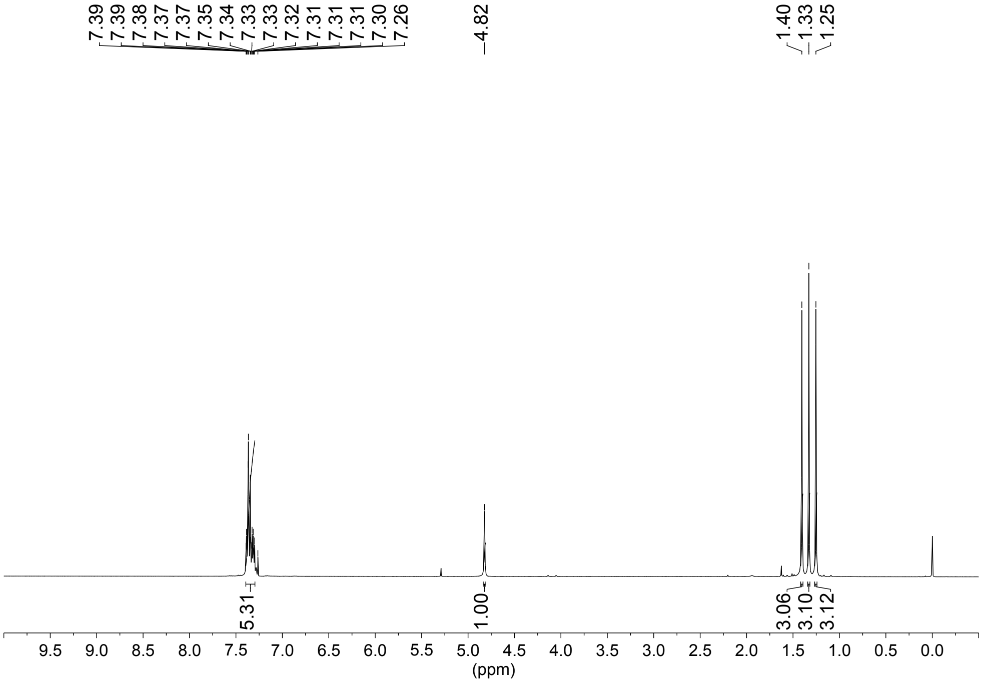


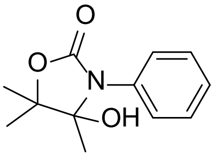
4d ^{13}C NMR ($CDCl_3$, 100.6 MHz)



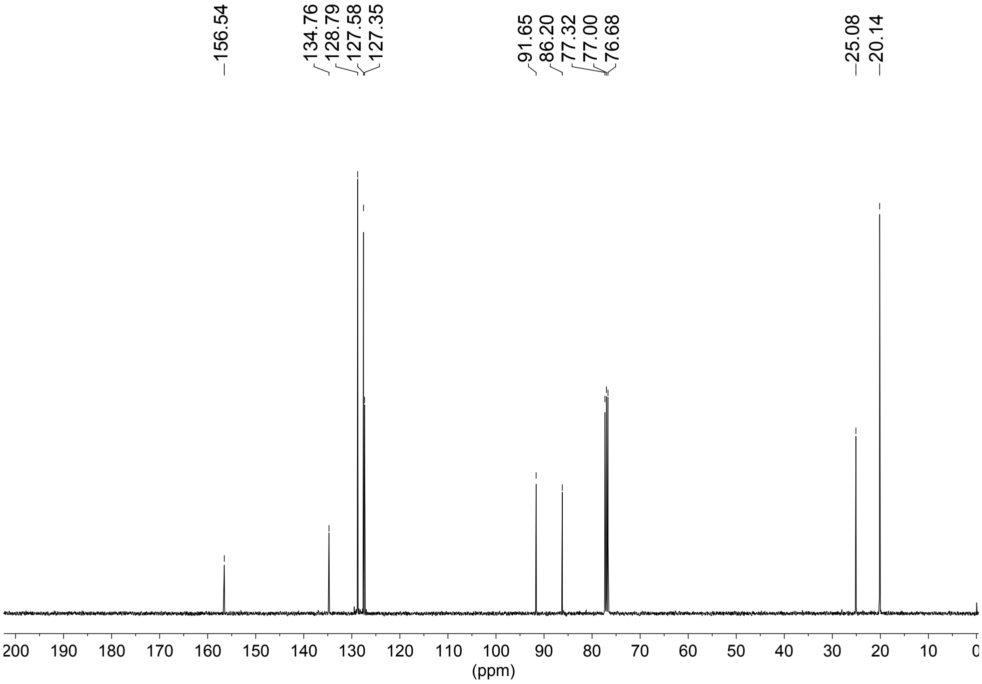


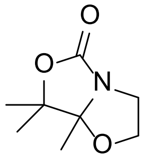
4e ^{1}H NMR ($CDCl_3$, 400 MHz)



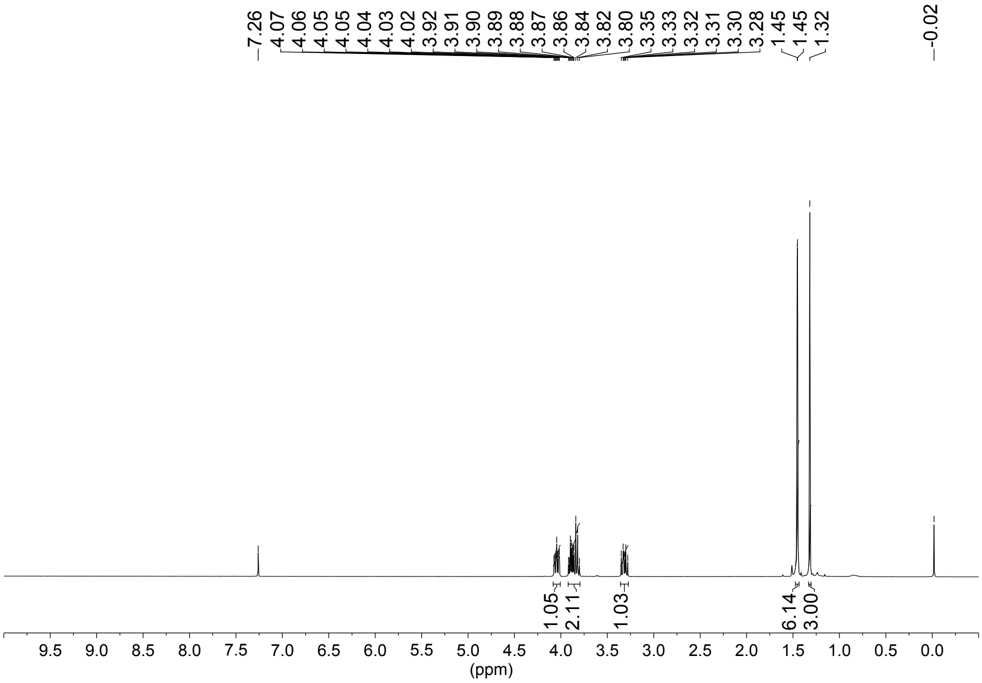


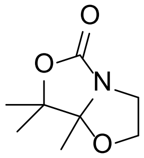
4e ^{13}C NMR ($CDCl_3$, 100.6 MHz)



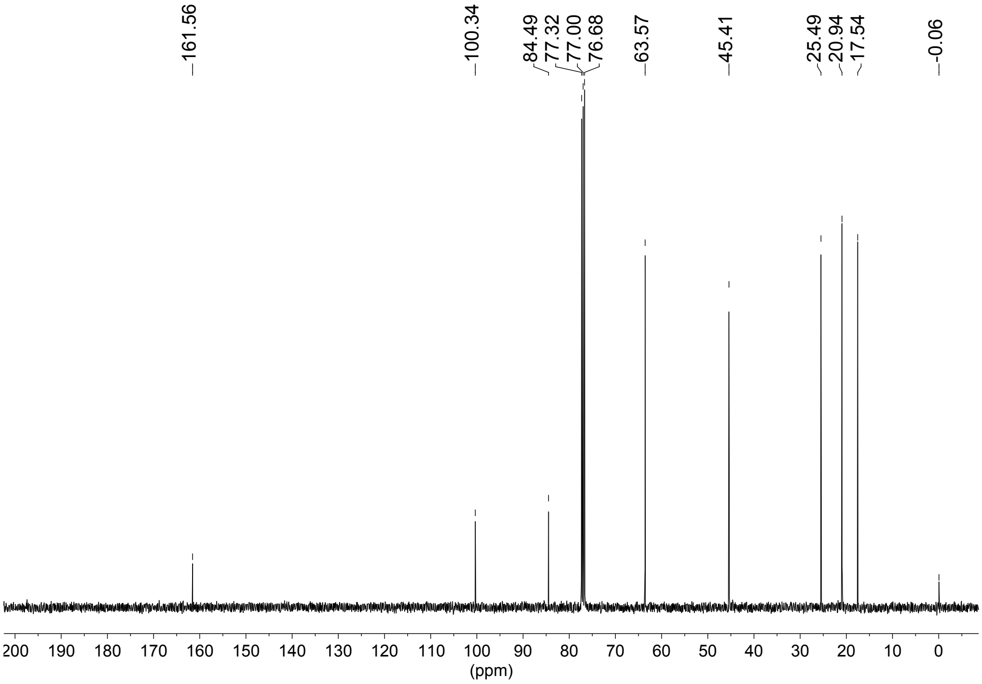


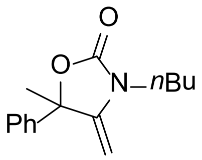
4f ^{1}H NMR ($CDCl_3$, 400 MHz)



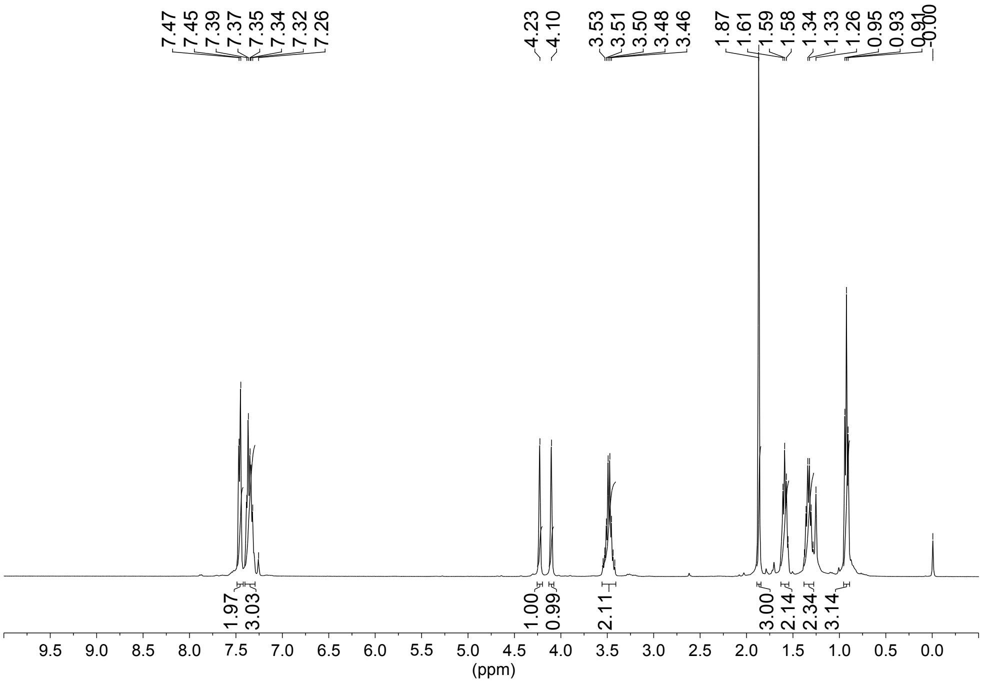


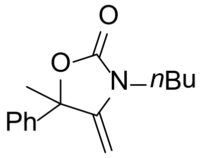
4f ^{13}C NMR ($CDCl_3$, 100.6 MHz)



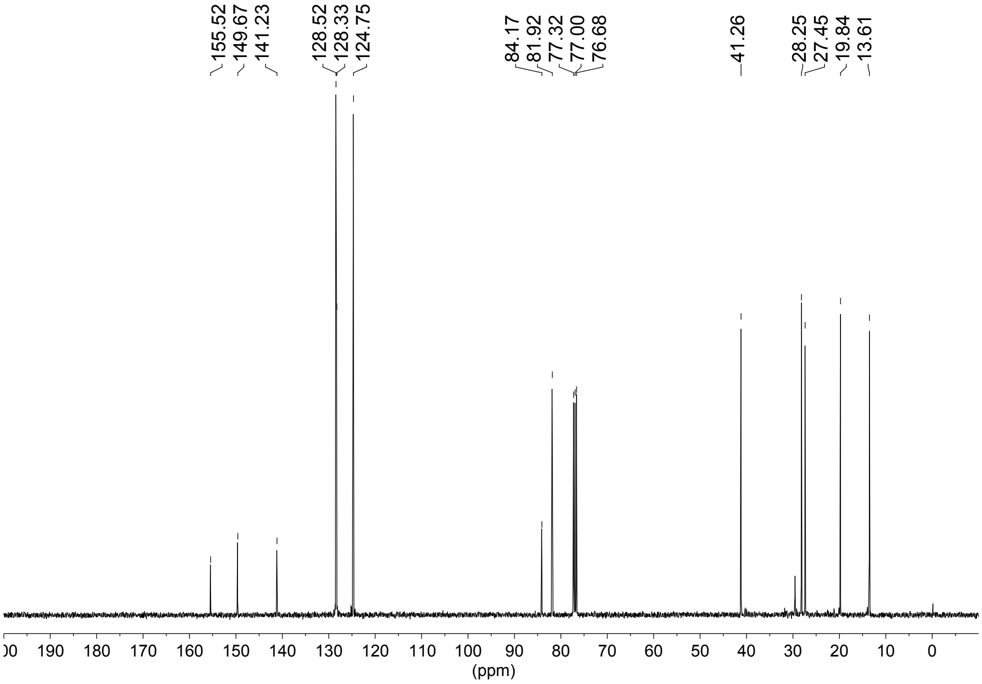


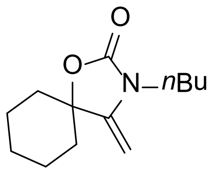
4g ^{1}H NMR ($CDCl_3$, 400 MHz)



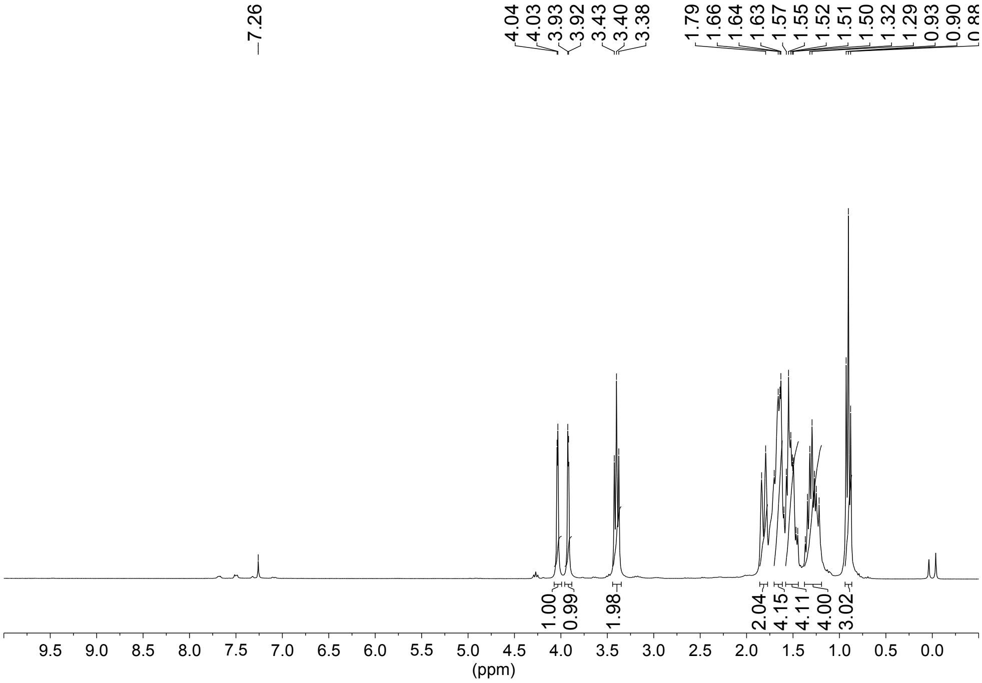


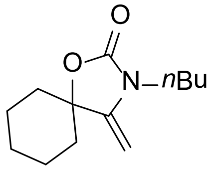
4g ^{13}C NMR ($CDCl_3$, 100.6 MHz)



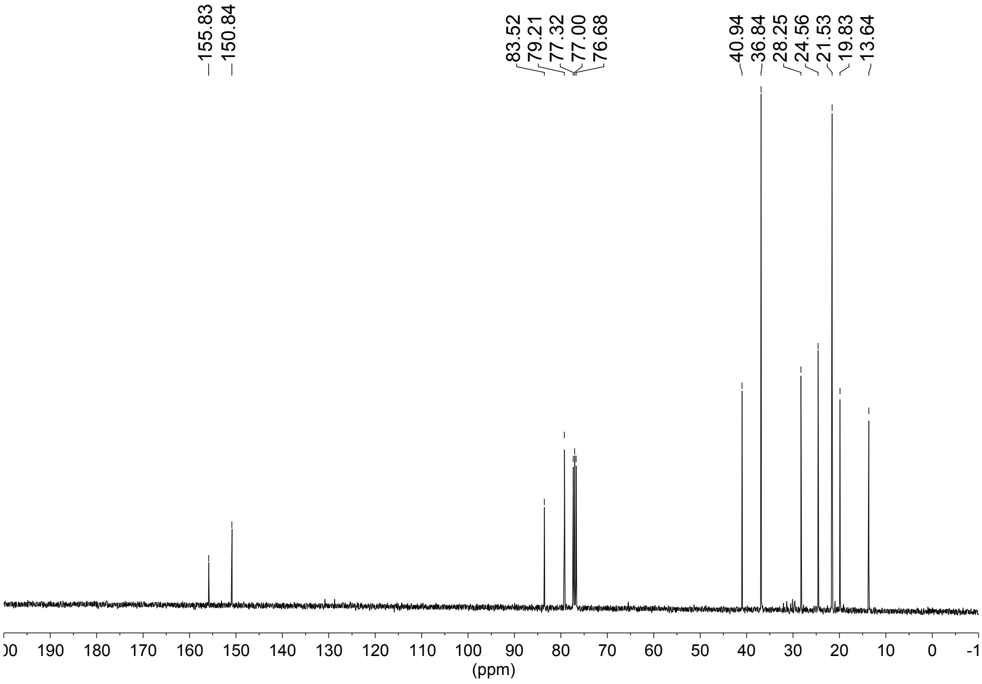


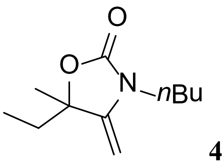
4h ^{1}H NMR ($CDCl_3$, 400 MHz)



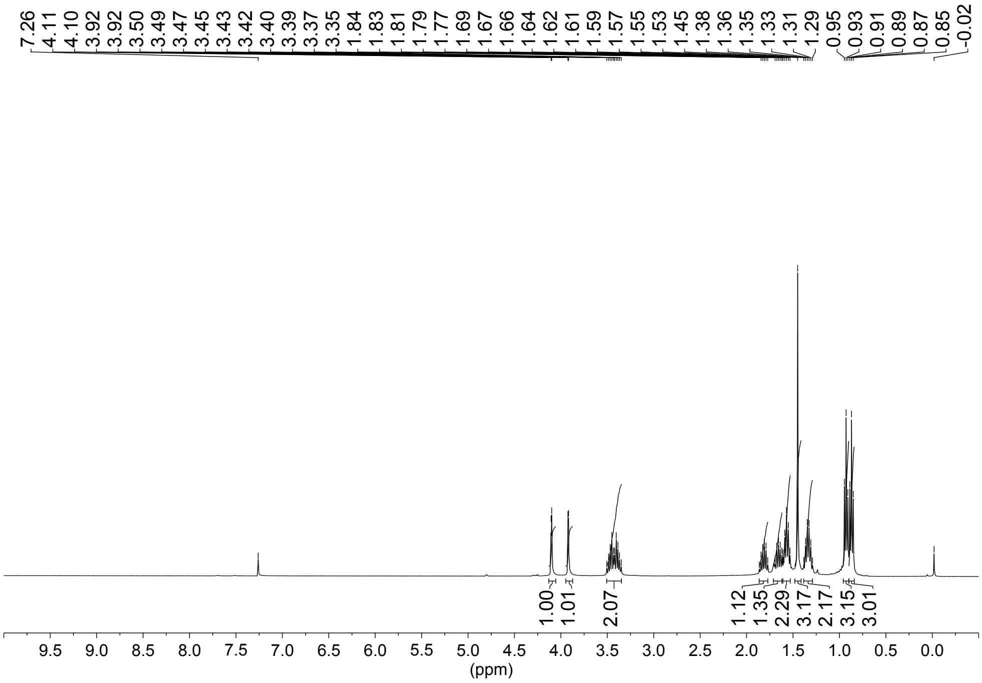


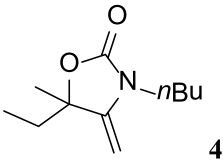
4h ^{13}C NMR ($CDCl_3$, 100.6 MHz)



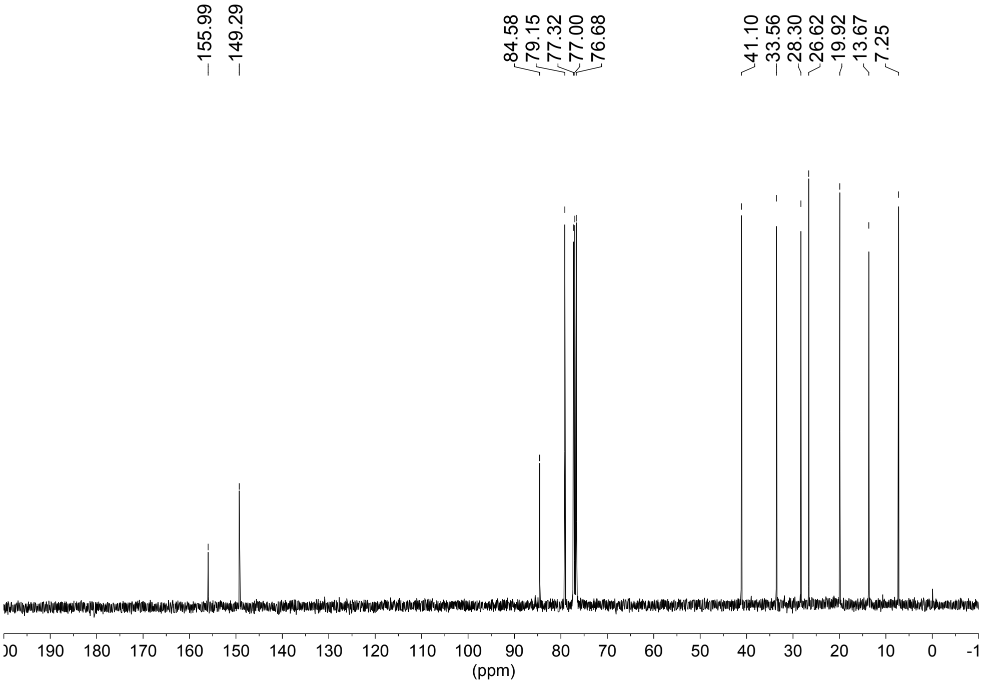


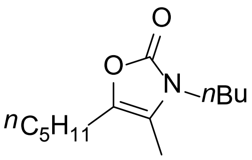
4i ^{1}H NMR (CDCl$_3$, 400 MHz)



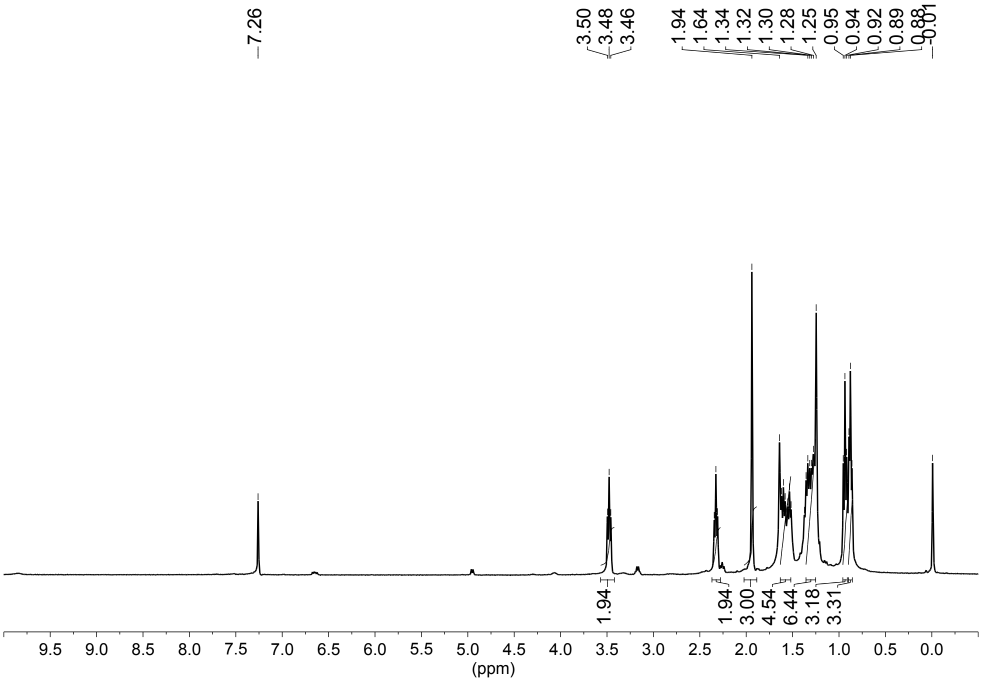


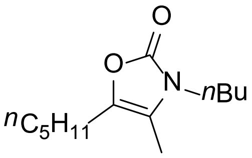
4i ^{13}C NMR (CDCl$_3$, 100.6 MHz)



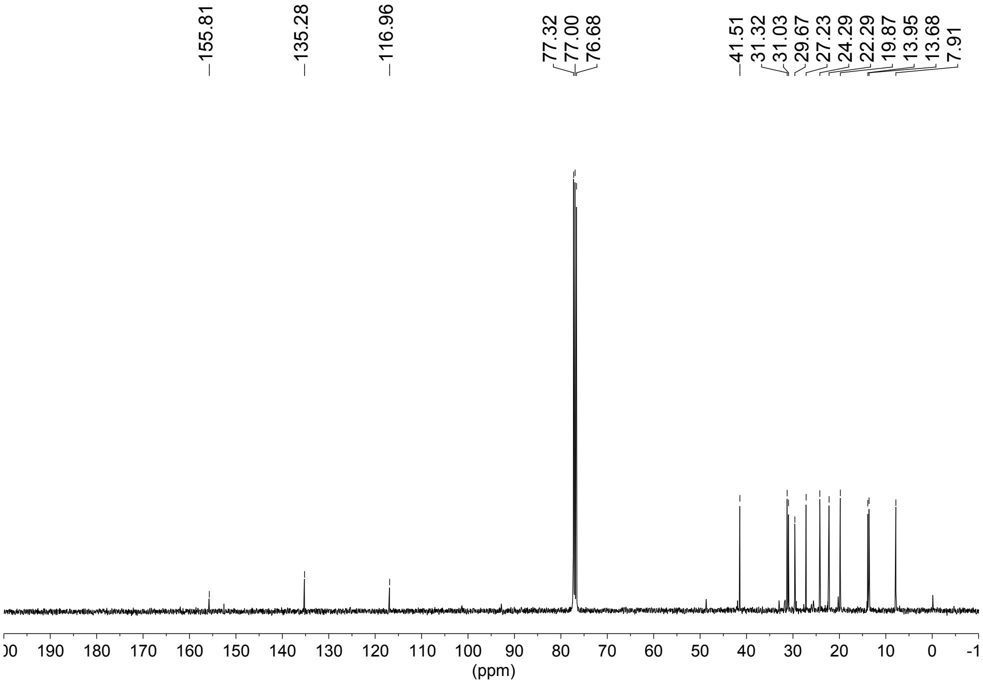


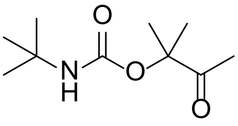
4j ^{1}H NMR ($CDCl_3$, 400 MHz)



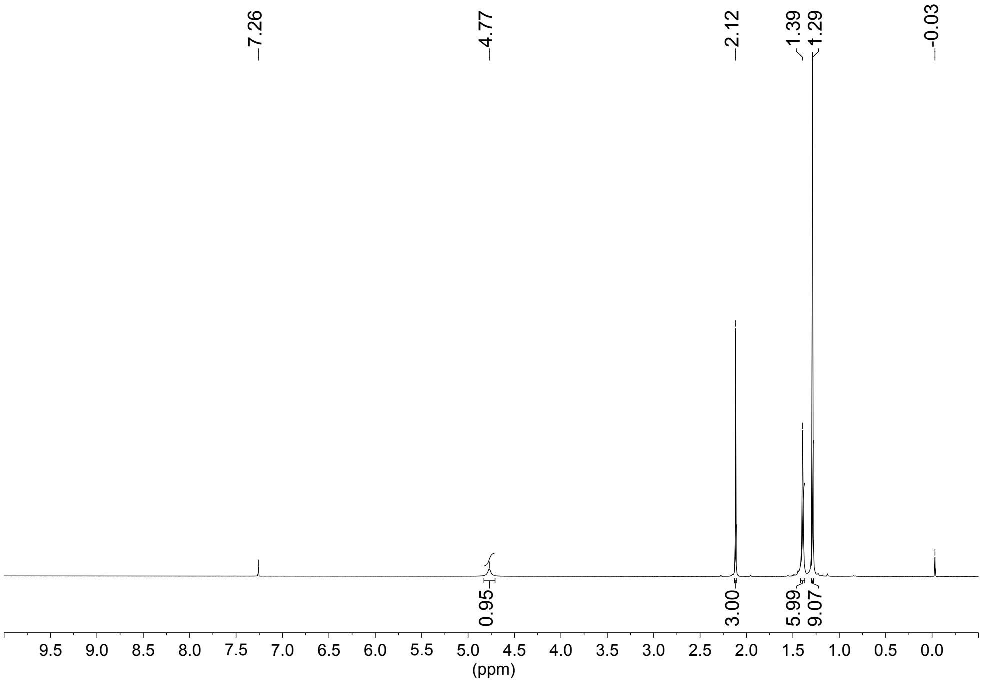


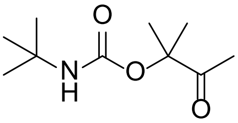
4j ^{13}C NMR ($CDCl_3$, 100.6 MHz)



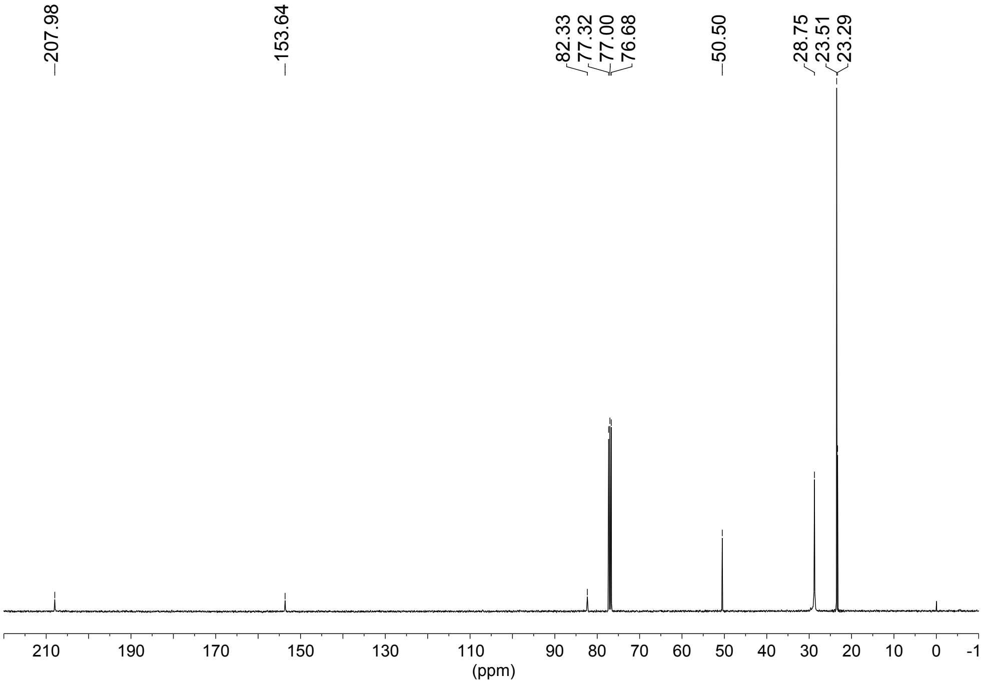


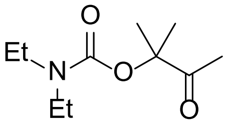
4k ^{1}H NMR ($CDCl_3$, 400 MHz)



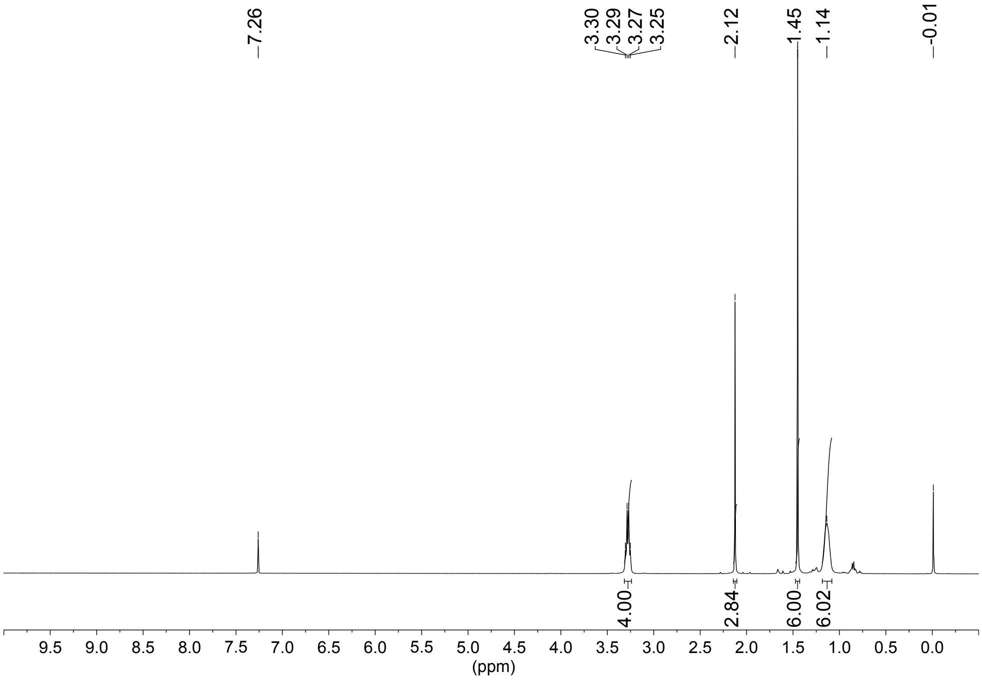


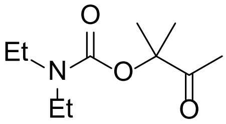
4k ^{13}C NMR ($CDCl_3$, 100.6 MHz)



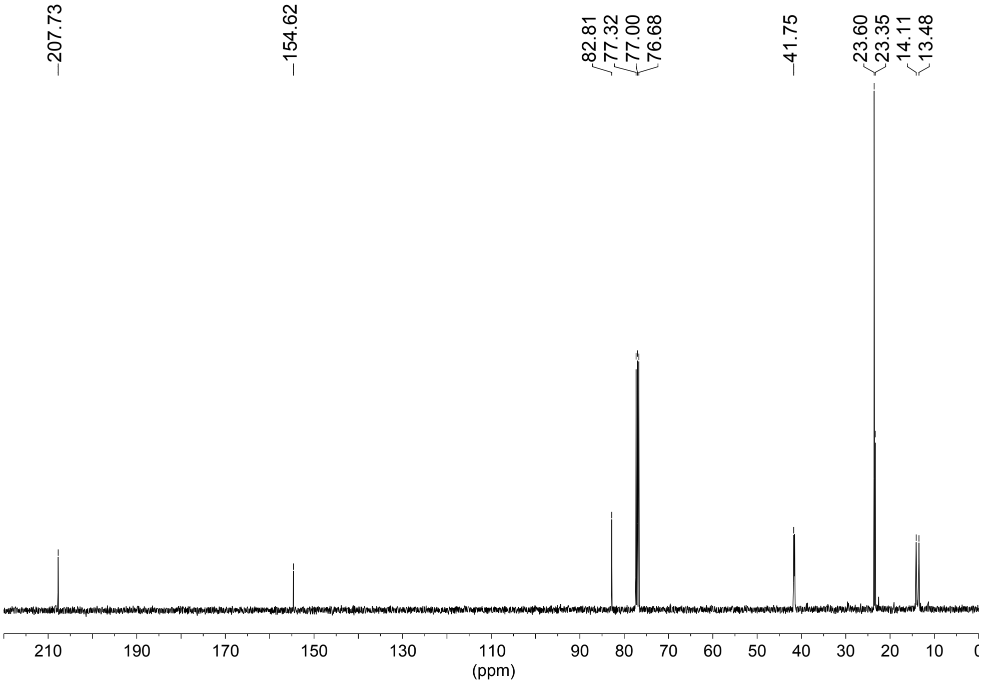


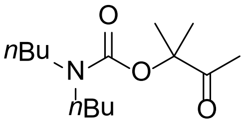
6a ^{1}H NMR ($CDCl_3$, 400 MHz)



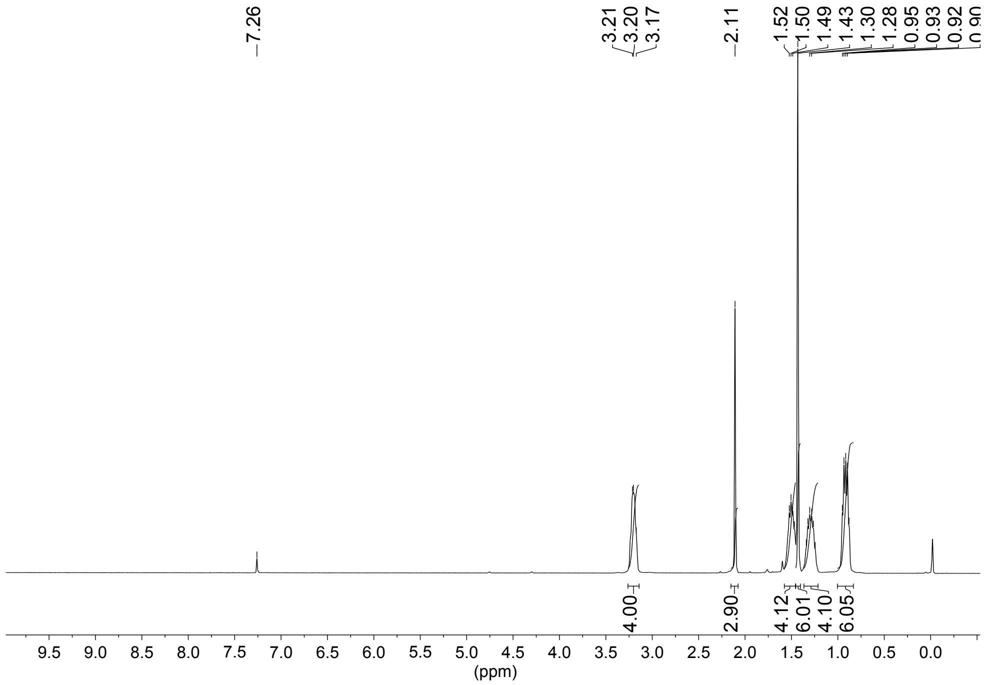


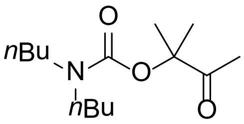
6a ^{13}C NMR ($CDCl_3$, 100.6 MHz)



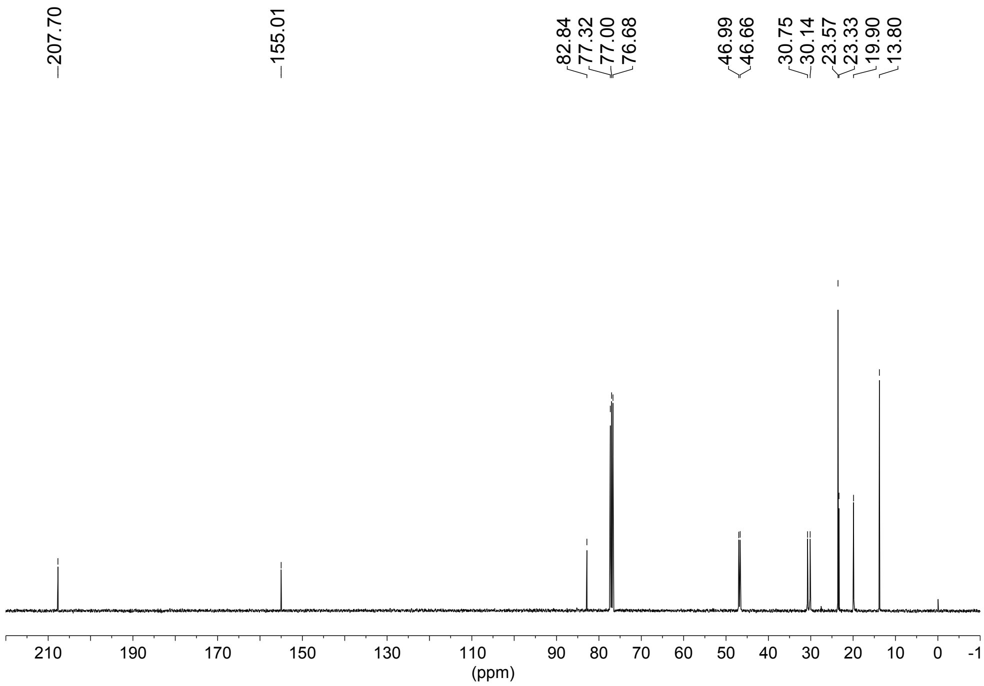


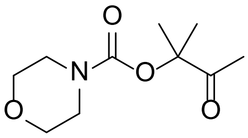
6b ^{1}H NMR ($CDCl_3$, 400 MHz)



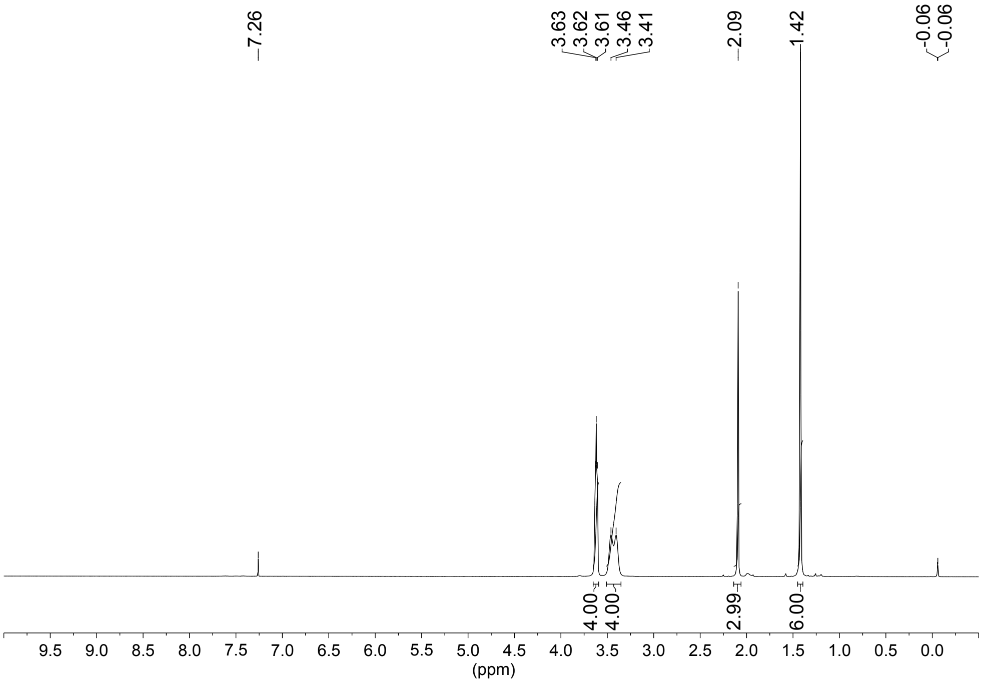


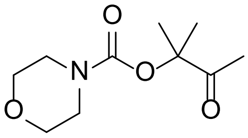
6b ^{13}C NMR ($CDCl_3$, 100.6 MHz)



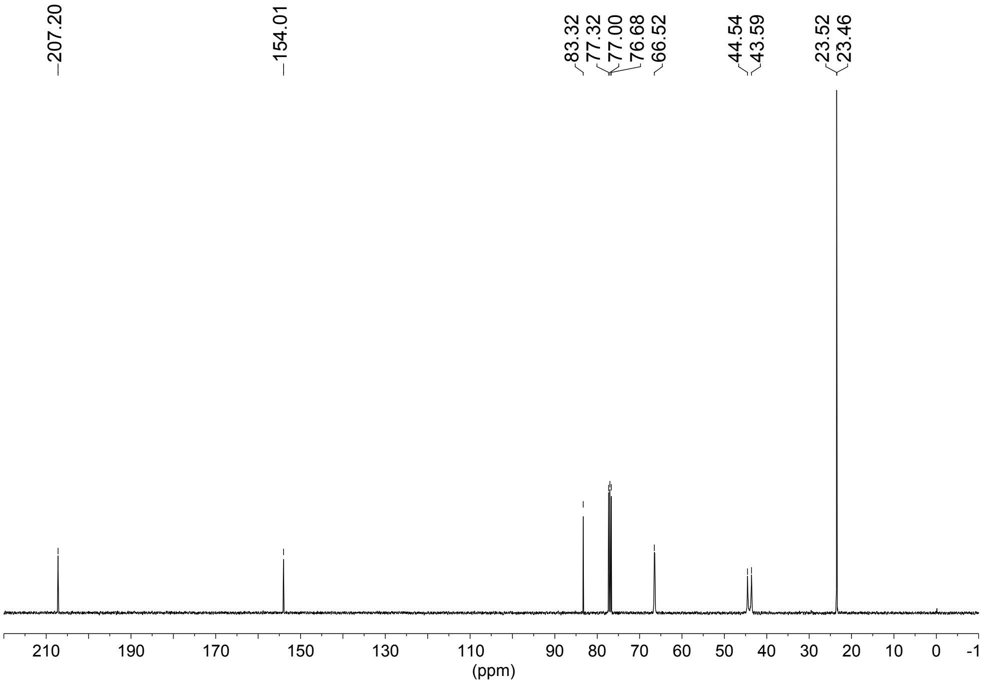


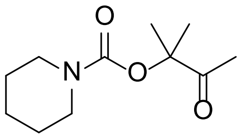
6c ^{1}H NMR (CDCl$_3$, 400 MHz)



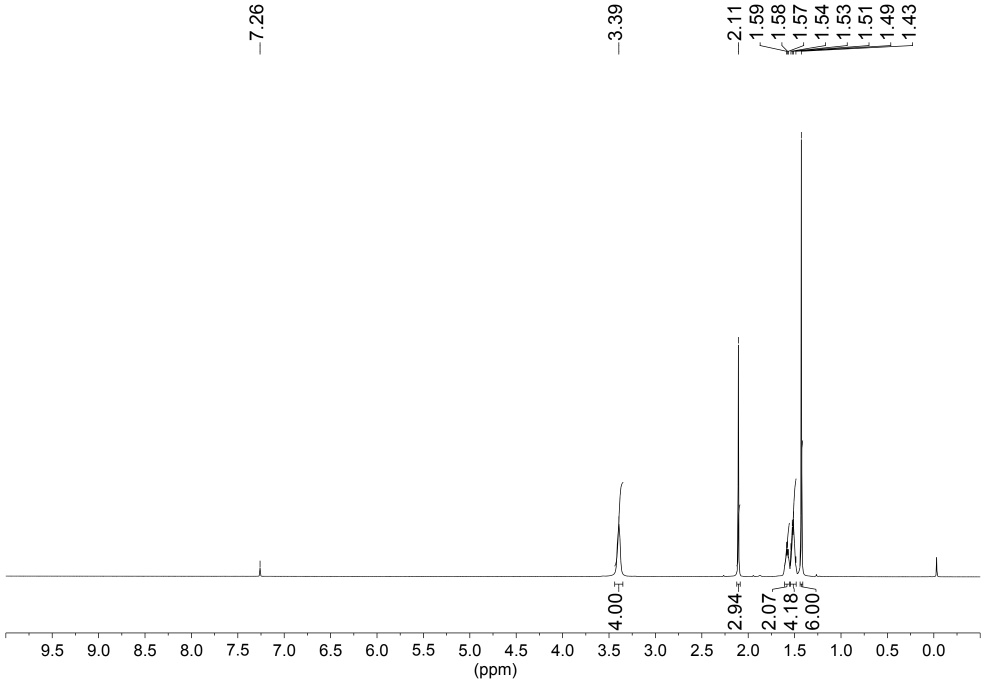


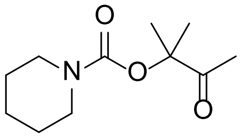
6c ^{13}C NMR (CDCl$_3$, 100.6 MHz)



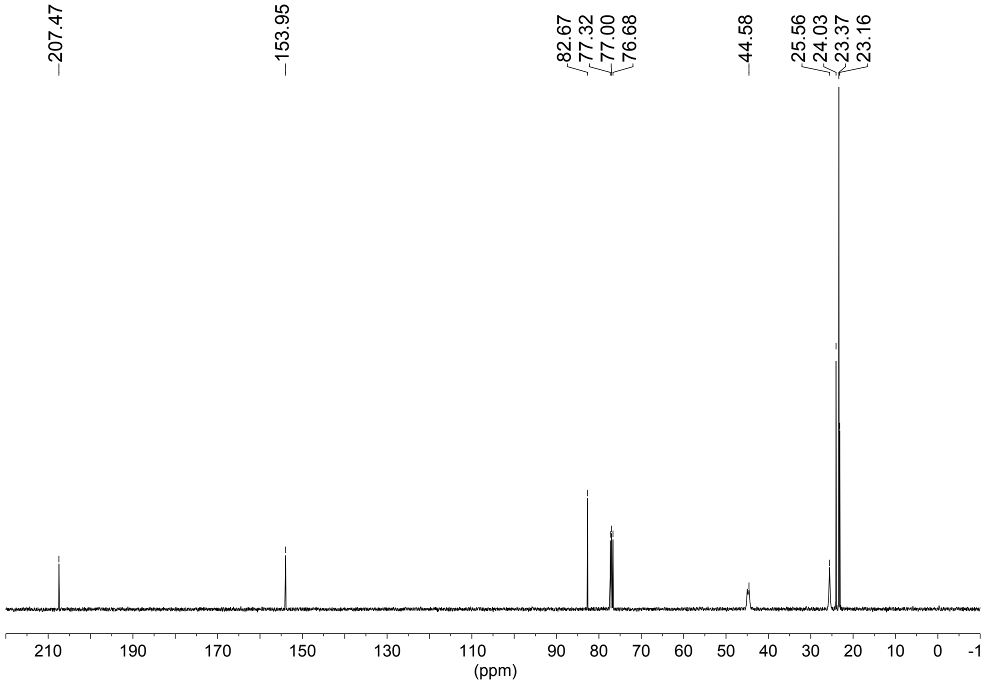


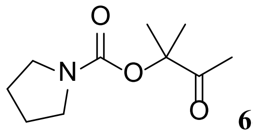
6d ^{1}H NMR ($CDCl_3$, 400 MHz)



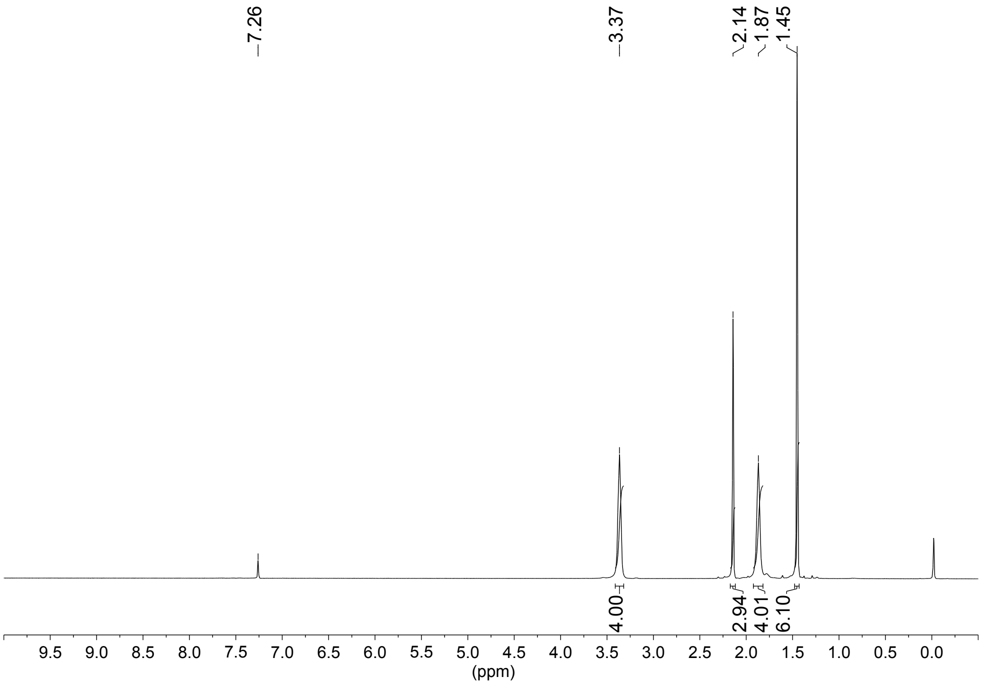


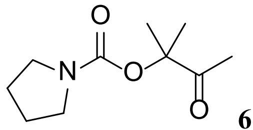
6d ^{13}C NMR ($CDCl_3$, 100.6 MHz)



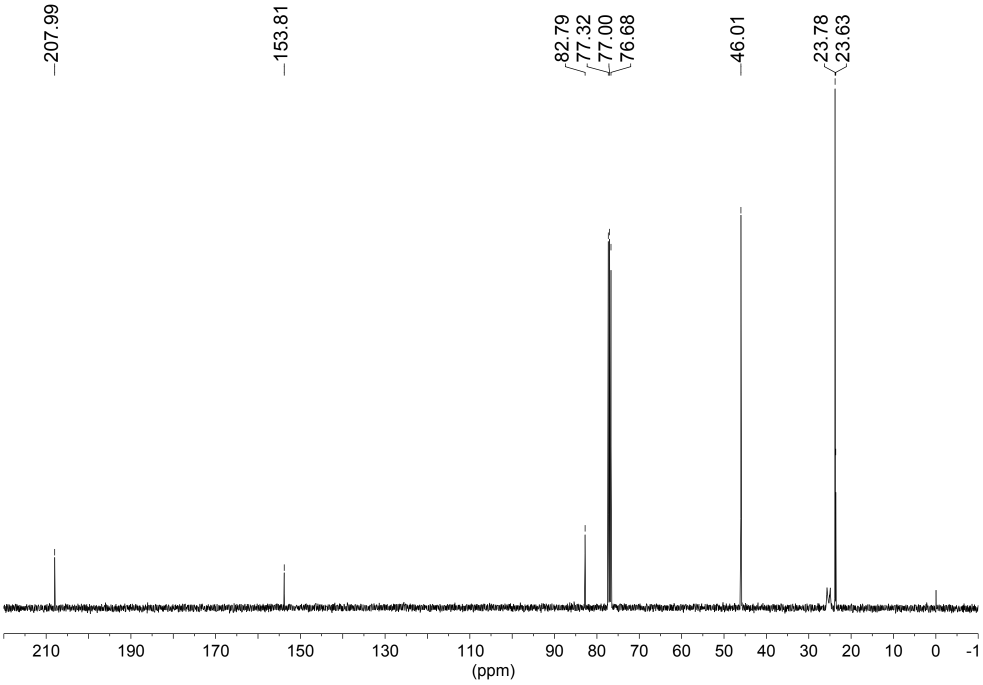


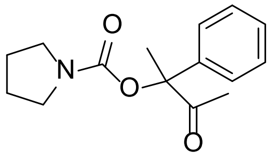
6e ^{1}H NMR ($CDCl_3$, 400 MHz)



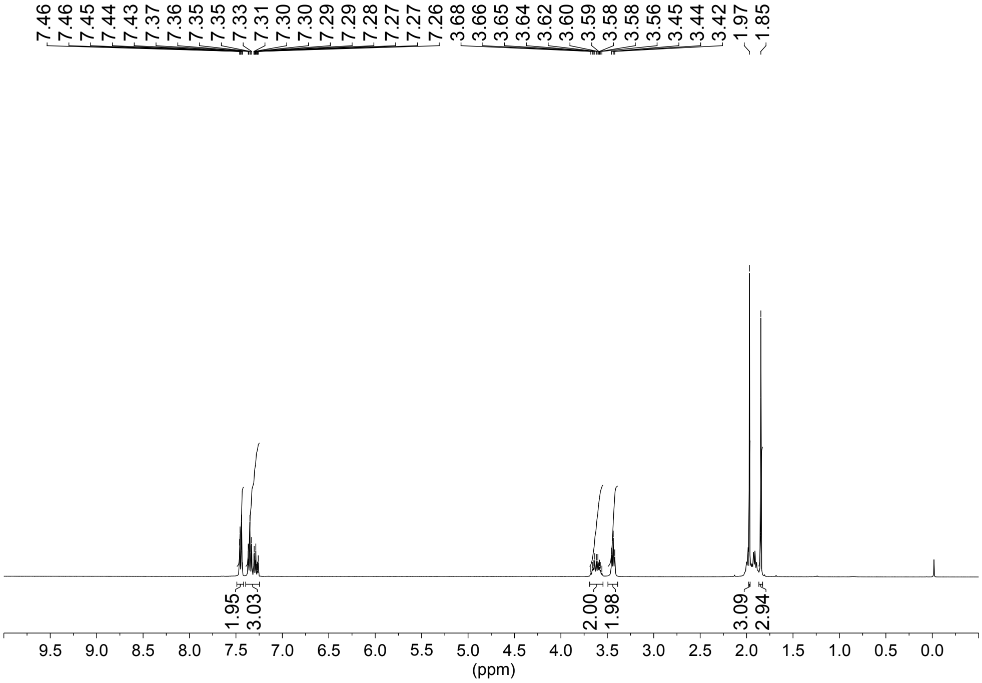


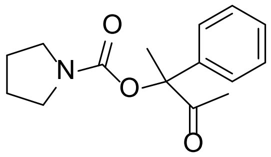
6e ^{13}C NMR ($CDCl_3$, 100.6 MHz)



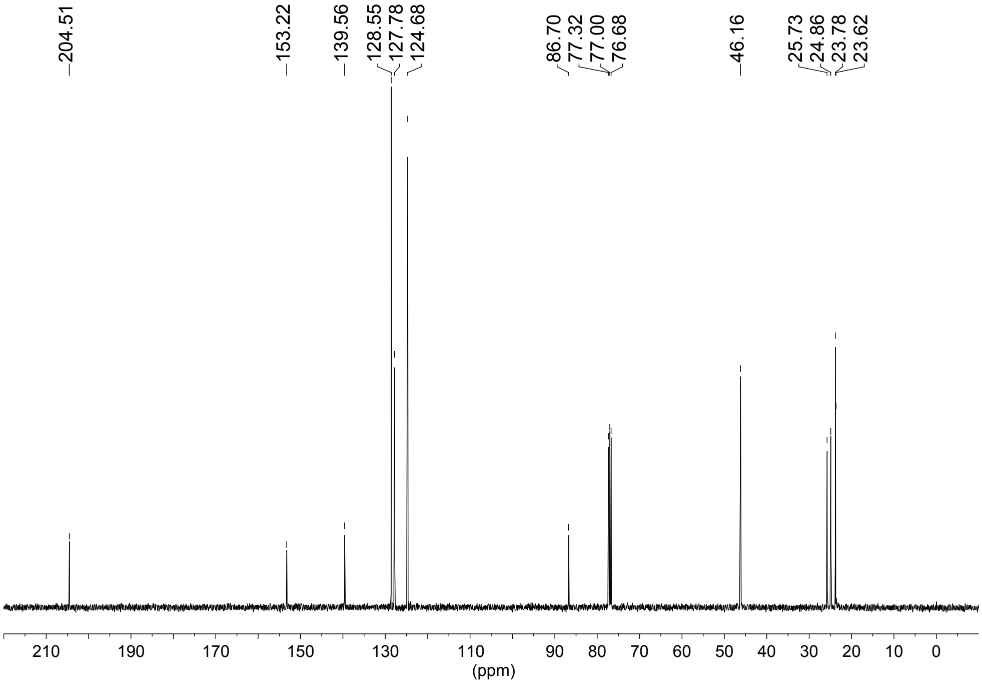


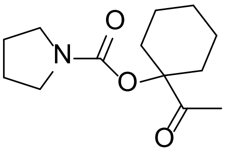
6f ^{1}H NMR ($CDCl_3$, 400 MHz)



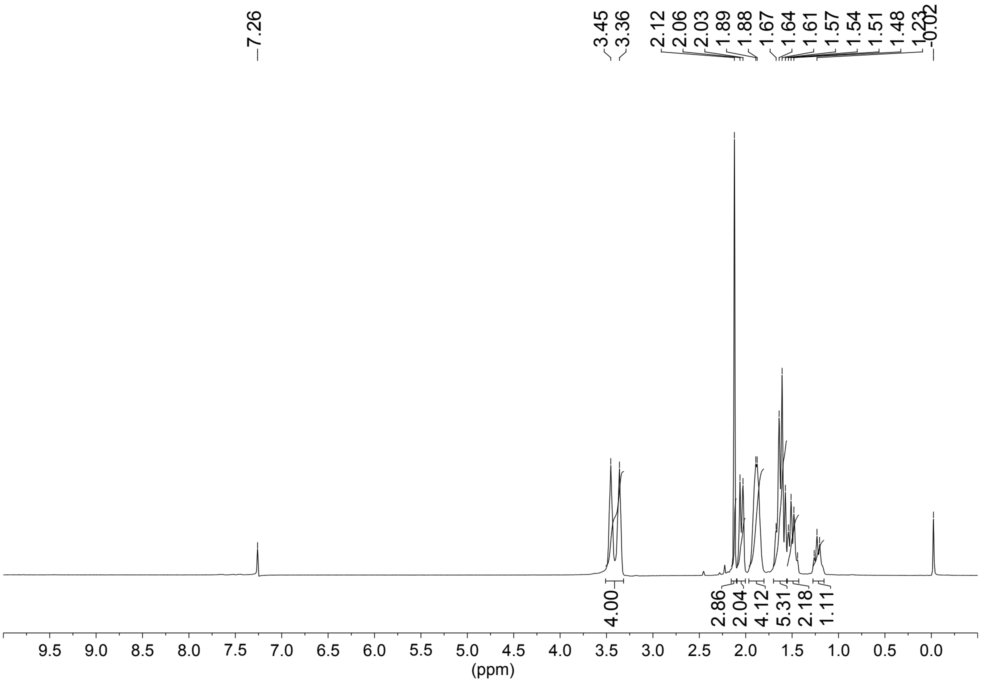


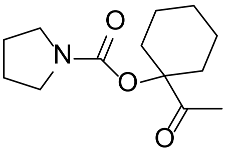
6f ^{13}C NMR ($CDCl_3$, 100.6 MHz)



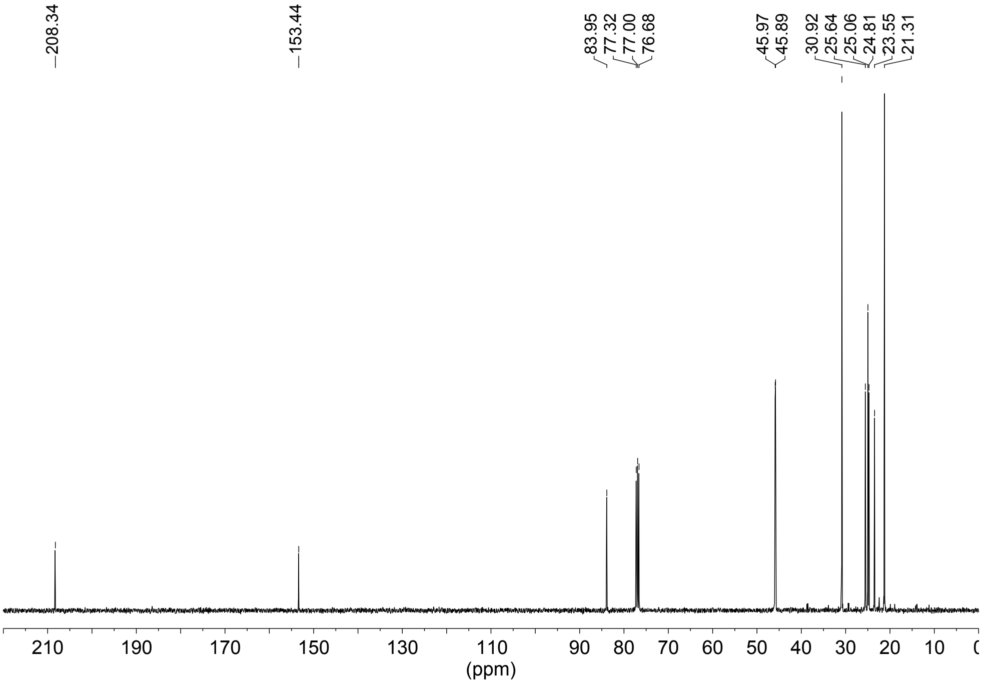


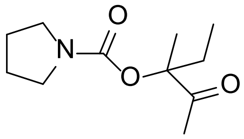
6g ^{1}H NMR ($CDCl_3$, 400 MHz)



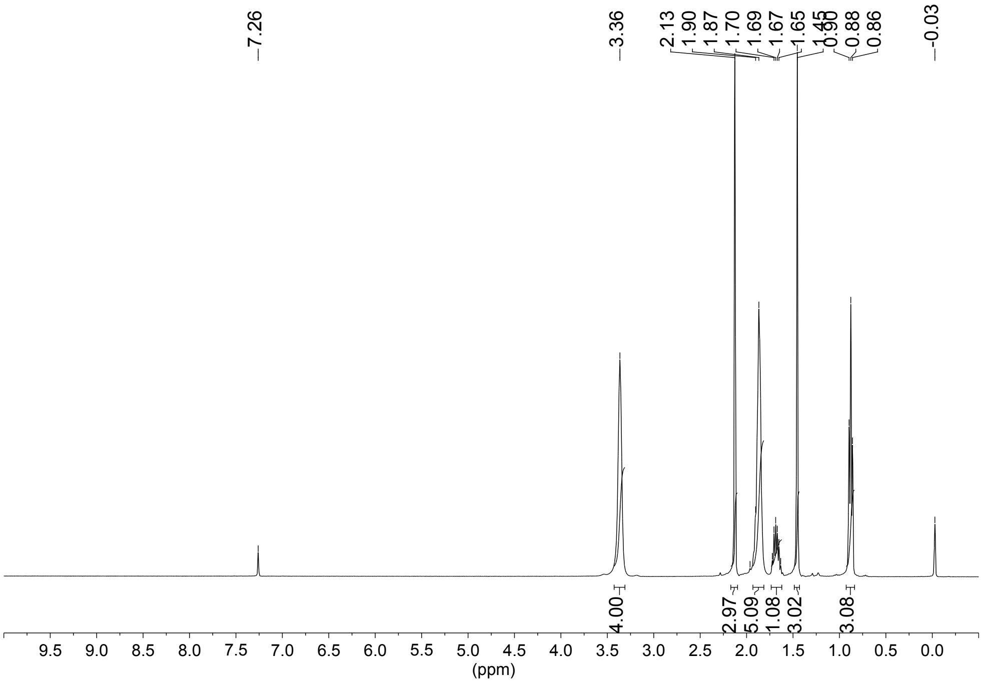


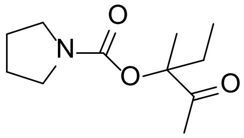
6g ^{13}C NMR ($CDCl_3$, 100.6 MHz)



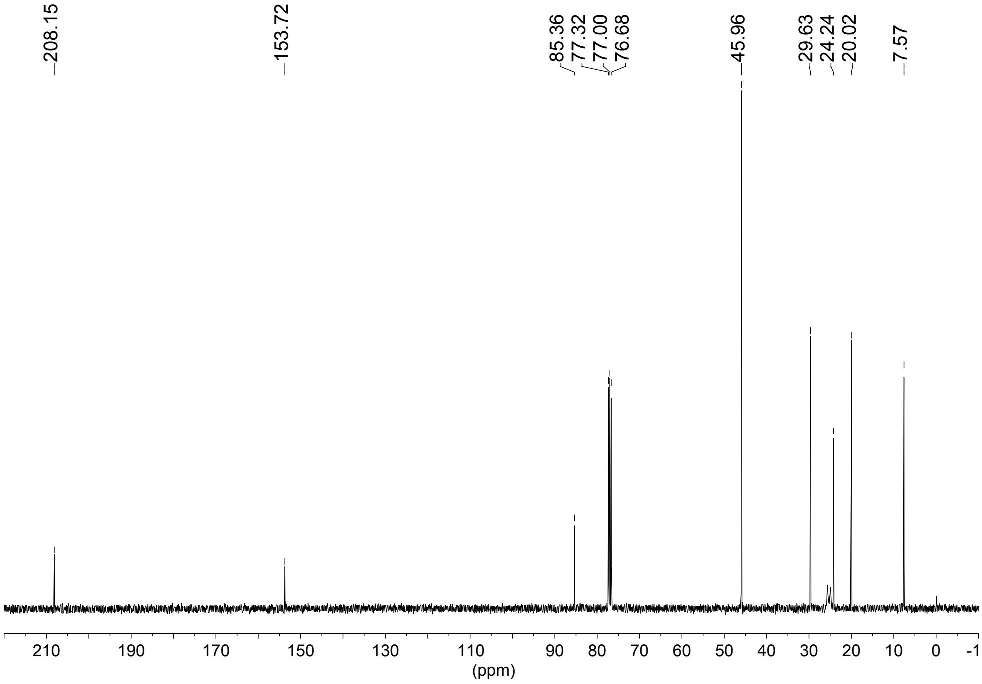


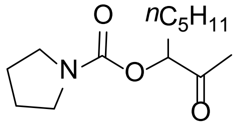
6h ^{1}H NMR (CDCl$_3$, 400 MHz)



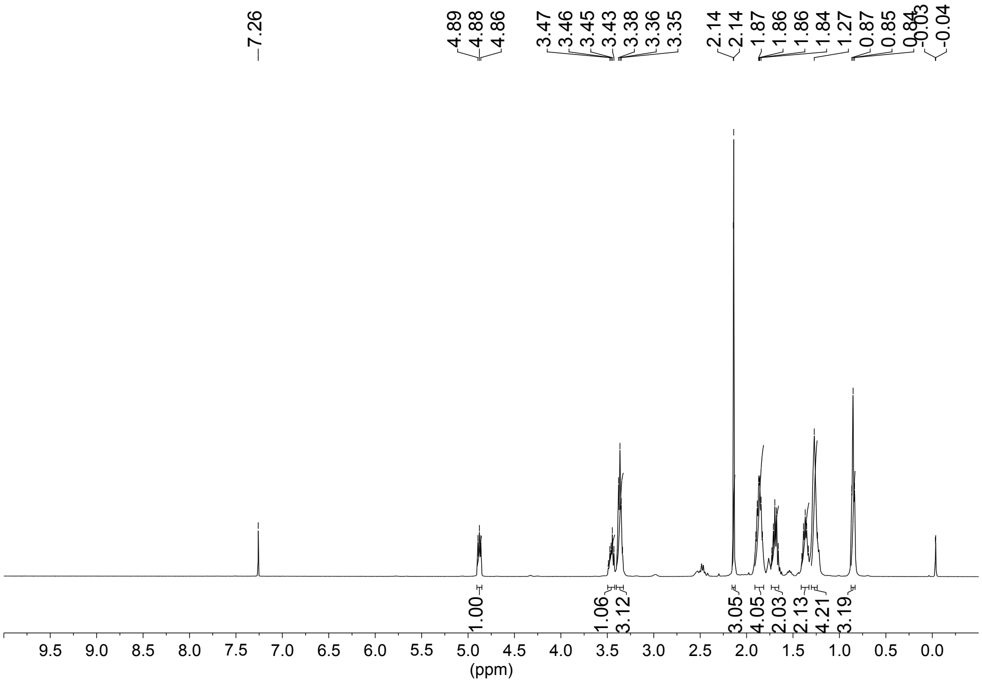


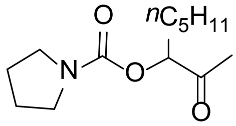
6h ^{13}C NMR (CDCl$_3$, 100.6 MHz)





6i ^{1}H NMR ($CDCl_3$, 400 MHz)





6i ^{13}C NMR ($CDCl_3$, 100.6 MHz)